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KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN TE AMSTERDAM.

PROCEEDINGS OF THE MEETING of Saturday May 31, 1902.

(Translated from: Verslag van de gewone vergadering der Wis- en Natuurkundige
Afdeeling van Zaterdag 31 Mei 1902, Dl. XI).

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The following papers were read:

Physics. — „*Ternary systems.*” IV. By Prof. J. D. VAN DER WAALS.
(Continued from Vol. IV pag. 694).

B. If we put $T = \text{constant}$ in equation I of our previous communication, we find the relation between dp , dx_1 and dy_1 at constant temperature in the following form:

$$v_{21} dp = \left\{ (x_2 - x_1) \frac{\partial^2 \xi}{\partial x_1^2} + (y_2 - y_1) \frac{\partial^2 \xi}{\partial x_1 \partial y_1} \right\} dx_1 + \\ + \left\{ (x_2 - x_1) \frac{\partial^2 \xi}{\partial x_1 \partial y_1} + (y_2 - y_1) \frac{\partial^2 \xi}{\partial y_1^2} \right\} dy_1 \quad \dots \dots (II)$$

For a binary system this relation is simplified to:

$$v_{21} dp = (x_2 - x_1) \frac{\partial^2 \zeta}{\partial x_1^2} dx_1 .$$

We know from the properties of a binary system, that we have then a curve $p = f(x_1)$ and a curve $p = f(x_2)$, and that the branch representing liquid phases is always found higher than the one representing vapour phases. Both curves start at the point representing the vapour-tension of the first component, and finish at the corresponding point for the second component. This however is only true if the temperature is lower than T_{cr} of that component. If $T > (T_{cr})_2$ then the two curves are joined fluently so that they form a single one.

For a ternary system we have to deal with two surfaces $p = f(x_1, y_1)$ and $p = f(x_2, y_2)$ instead of the curves $p = f(x_1)$ and $p = f(x_2)$. We will use as a rule the index 1 for a liquid phasis, the index 2 for a vapour phasis. These surfaces cover the rectangular triangle OXY , and above the angles of this triangle they have points in common. The common ordinates represent the maximum tensions of the three components. This holds good, if the temperature is lower than T_{cr} of each of the components. In some cases these sheets may have still another point in common, just as is the case with the two branches for a binary mixture if a maximum pressure occurs. But for the present we will disregard the existence of such a maximum pressure. If $T < T_{cr}$ of one of the components then the two sheets of the p -surface do not cover any longer the whole rectangular triangle, but they have joined fluently to one surface.

In the above equation II the properties of these two sheets of the p -surface are expressed in the form of a differential equation; — we will now proceed to deduce the principal properties from this equation. Even for the pressure-curves of a binary mixture the number of these properties is already considerable. For a ternary system they will of course be still much more numerous, and even properties occur which have no analogon for a binary system. But many of the properties of the pressure-curves of a binary mixture may directly be extended to the corresponding ones for the pressure surfaces of a ternary mixture. Such properties need hardly be treated here, as we suppose the properties of a binary mixture to be known. Accordingly I will limit myself in the main to treating those properties that are proper to ternary systems but not to binary systems. The study of the ternary systems however has induced me, to give a more detailed discussion of some equations, given in Cont. II for a binary mixture, from a more general point of view. And in some cases this detailed

discussion has enabled me to give a more precise and accurate form to some of the equations and to some of the quantities occurring in them. In these cases I shall discuss some properties more extensively, concerning which I had else confined myself to refer to Cont. II.

From a theoretical point of view the relation between p , x_1 and y_1 at given temperature is not more important than that between v_1 , x_1 and y_1 or between v_2 , x_1 and y_1 . But even for a simple substance the experimental investigation concerning the maximum pressure has first been executed, and only in these later years it has been followed by an investigation concerning the densities. In the same way we may expect, that also for a ternary system the experiment will occupy itself in the first place with the determination of the pressure, and that the investigation as to the densities of the phases coexisting with other phases, will follow later. The surface representing for all temperatures the pressure as function of the composition of a binary mixture has been called by me "surface of saturation". We might call for a ternary system the surface whose properties we are about to investigate "surface of saturation for a given temperature". Wherever it is not ambiguous I shall speak simply of "surface of saturation".

In the following considerations we will take triangle OXY in a horizontal plane; the direction in which the pressure is laid off is then vertical. We represent the maximum pressures of the three components by p_1 , p_2 and p_3 where we choose the indices in such a way that

$$p_1 < p_2 < p_3.$$

If $T > T_{cr}$ for one of the components, then the surface of saturation does not reach the corresponding angle and the corresponding maximum pressure does not exist any longer.

a. Curves of equal pressure.

For curves of equal pressure, we have $dp = 0$, and equation II is reduced to:

$$\left\{ (x_2 - x_1) \frac{\partial^2 \xi}{\partial x_1^2} + (y_2 - y_1) \frac{\partial^2 \xi}{\partial x_1 \partial y_1} \right\} dx_1 + \\ + \left\{ (x_2 - x_1) \frac{\partial^2 \xi}{\partial x_1 \partial y_1} + (y_2 - y_1) \frac{\partial^2 \xi}{\partial y_1^2} \right\} dy_1 = 0.$$

The projection of these curves is of course the same as the projection of the connodal curve of the ξ -surface construed for this pressure. We have discussed this projection in our first communication p. 461. If p is chosen such that $p_1 < p < p_3$, the two branches of this projection cut the two sides of the triangle adjacent

to the right angle. If $p_2 < p < p_3$ then they cut the hypotenuse and the other side corresponding with the third component. If $p = p_2$ then the two branches cut one another in the angle of the second component. We might find the equation of these curves if we could express x_2 and y_2 in x_1 and y_1 , and if $\frac{\partial^2 \xi}{\partial x_1^2}$, $\frac{\partial^2 \xi}{\partial x_1 \partial y_1}$ and $\frac{\partial^2 \xi}{\partial y_1^2}$ were known. And though this is not completely possible in all cases, yet in some cases we may find the equation approximately. A digression in order to discuss these quantities cannot be left out here; else we shall always be confronted with the same unanswered questions in all subsequent problems.

The value of ξ is given p. 449, vol. IV, in the following form:

$$\xi = MRT \{ (1-x-y) \log (1-x-y) + x \log x + y \log y \} + pv - \int p dv.$$

We omit the linear function of x and y , as it has no influence on the phenomena of equilibrium. So the value of ξ consists of a pure function of x and y , and of another part which fulfils the well known condition:

$$(d\xi)_{xyT} = v dp.$$

This second part is known if the equation of state is known. In fig. 1, p. 450 I have represented graphically this second part such as we may conclude its course to be if we only assume the principle of continuity. In what follows we will extend the principle of continuity so far, that we assume the equation of state to vary fluently if x and y vary fluently. We now imagine the second part of ξ to be construed for all mixtures, i. e. for all values of x and y , and for all values of p . If we now put $p = \text{constant}$, then we have an auxiliary quantity, which varies with x and y , and the knowledge of whose properties is the condition for the solving of all questions relating to the equilibrium, either of a binary, or of a ternary mixture, or of any system of still more components. As we have already stated the knowledge of this quantity depends on the knowledge of the equation of state. From this appears, how absurd the opinion is, that knowledge of the equation of state would not be required for the knowledge of these systems. Yet we find this opinion often expressed. For the knowledge of the equilibrium of a simple substance it would be required, but for much more complicated systems it would be totally superfluous! I have introduced this auxiliary quantity already before (see i. a. *Cont.* II, p. 147); I shall represent by μ the quotient, obtained by dividing it by MRT . Now we have:

$$\xi = MRT \{ (1-x-y) \log (1-x-y) + x \log x + y \log y + \mu \}.$$

From this follows

$$\begin{aligned} \left(\frac{d\xi}{dx} \right)_{p,T,y} &= MRT \left\{ \log \frac{x}{1-x-y} + \left(\frac{d\mu}{dx} \right)_{p,T,y} \right\} \\ \left(\frac{d\xi}{dy} \right)_{p,T,x} &= MRT \left\{ \log \frac{y}{1-x-y} + \left(\frac{d\mu}{dy} \right)_{p,T,x} \right\} \\ \left(\frac{d^2\xi}{dx^2} \right)_{p,T,y} &= MRT \left\{ \frac{1-y}{x(1-x-y)} + \left(\frac{d^2\mu}{dx^2} \right)_{p,T,y} \right\} \\ \left(\frac{d^2\xi}{dx dy} \right)_{p,T} &= MRT \left\{ \frac{1}{1-x-y} + \left(\frac{d^2\mu}{dx dy} \right)_{p,T} \right\} \\ \left(\frac{d^2\xi}{dy^2} \right)_{p,T,x} &= MRT \left\{ \frac{1-x}{y(1-x-y)} + \left(\frac{d^2\mu}{dy^2} \right)_{p,T,x} \right\}. \end{aligned}$$

For brevity's sake I shall represent $\left(\frac{d\mu}{dx} \right)_{p,T,y}$ by μ'_x . With analogous signification the symbols μ'_y , μ''_x , μ''_{xy} and μ''_y will be used.

We deduce from the conditions of coexistence (see p. 551, 553 and 554 Vol. IV) the following relations.

$$\text{From } \left(\frac{d\xi}{dx} \right)_1 = \left(\frac{d\xi}{dx} \right)_2 \text{ follows } \frac{x_1}{1-x_1-y_1} e^{\mu'_x} = \frac{x_2}{1-x_2-y_2} e^{\mu'_x} \quad . \quad (1)$$

$$\text{From } \left(\frac{d\xi}{dy} \right)_1 = \left(\frac{d\xi}{dy} \right)_2 \text{ follows } \frac{y_1}{1-x_1-y_1} e^{\mu'_y} = \frac{y_2}{1-x_2-y_2} e^{\mu'_y} \quad . \quad (2)$$

$$\text{And from } \left\{ \xi - x \frac{d\xi}{dx} - y \frac{d\xi}{dy} \right\}_1 = \left\{ \xi - x \frac{d\xi}{dx} - y \frac{d\xi}{dy} \right\}_2 \text{ follows:}$$

$$\{ \log (1-x_1-y_1) + \mu_1 - x_1 \mu'_{x_1-y_1} \mu_{y_1} \} = \{ \log (1-x_2-y_2) + \mu_2 - x_2 \mu'_{x_2-y_2} \mu_{y_2} \} \quad (3).$$

From these equations (1), (2) and (3) again follows, that we can express the relation between the composition of the coexisting phases only then, if we know what variation in the equation of state is caused by the substitution of one of the components by another. So we find e. g. for the determination of the limiting value of the ratio of x_1 and x_2 in the case that x_1 and y_1 are infinitely small the equation:

$$\log \frac{x_2}{x_1} = \mu'_{x_1} - \mu'_{x_2} \quad .$$

If we exclude the knowledge of the equation of state, we can in nowise account for the considerable differences which this ratio shows

in different cases, and we have to consider it as a primary datum without any relation to other properties of the solvent or of the solved substance. Neither can we account for the value of this ratio, if we think that the application of the law of BOYLE is sufficient for the theory of mixtures; for this law is the same for all substances and cannot therefore account for the different values which this ratio has in different cases. Therefore it appears convincingly that a closer investigation of the quantities μ , μ'_x , μ'_y , μ''_x , μ''_{xy} and μ''_y is required. I pass now to this investigation.

We start from the following equation, which may be considered as the definition of the quantity under consideration:

$$MRT\mu = \int_0^p v dp$$

So in the first place this quantity depends on p , but as the equation of state for a mixture depends on the composition, it also depends on x and y . We deduce from this equation:

$$MRT\left(\frac{d\mu}{dx}\right)_{pT_y} = MRT\mu'_x = \int_0^p \left(\frac{dv}{dx}\right)_{pT_{v_1}} dp$$

If we write $\left(\frac{dv}{dx}\right)_p = -\left(\frac{\partial p}{\partial x}\right)_v \left(\frac{\partial v}{\partial p}\right)_x$, we find also:

$$MRT\mu'_x = - \int \left(\frac{\partial p}{\partial x}\right)_v \left(\frac{\partial v}{\partial p}\right)_x dp = - \int_{v=\infty}^v \left(\frac{\partial p}{\partial x}\right)_v dv$$

$$\text{or } MRT\mu'_x = \left(\frac{\partial \Psi}{\partial x}\right)_n$$

In Cont. II, p. 9 and p. 19 I have started from this last equation, and making use of the form of the equation of state given there, I have obtained the result, that for low temperatures μ'_{x_2} may be neglected and μ'_{x_1} may be put approximately proportional to $-\frac{dT_{cr}}{dx}$, if by the symbol T_{cr} we represent the temperature which would be the critical temperature of a liquid mixture, if this mixture might be considered as a simple substance; or, what comes to the same, T_{cr} represents that temperature for which the theoretical isothermal of that mixture which we think always homogeneous, presents only one horizontal tangent, and for which therefore maximum- and minimum-pressure have coincided.

It is true that this quantity T_{cr} is no experimental quantity, and

that we therefore might superficially think, that the introduction of T_{cr} is of no use; but in the first place in very many cases the critical temperatures, found experimentally, do not differ much from this quantity and in the second place even the simple assumption, that this quantity varies fluently with the composition, will yield many conclusions, confirmed by the experiments. As an instance I mention the connection of the fact, that if a mixture has a minimum critical temperature, a maximum-pressure is found on the connodal curve. A closer investigation of the signification of the quantity μ itself will however enable us to give a still more exact form to all further conclusions which have been deduced in this way, and to all further deductions which are important for the theory of mixtures. For the present I shall occupy myself only with the case that one of the coexisting phases is a rarefied gas-phase. In this case μ'_{x_2} and μ'_{y_2} may be neglected. For in the equation:

$$MRT\mu = \int^p v dp$$

the value of v may be represented by $\frac{MRT}{p}$ if the phases are very rare, and this holds for every mixture whatever its composition may be. Therefore we get by integration:

$$MRT\mu = MRT \log p + \varphi(T) .$$

In order to remain in accordance with the form of p. 450, I will determine $\varphi(T)$ such, that we may write:

$$\mu = \log \frac{p}{MRT} + 1 .$$

This signifies in fig. 1 that the vapour branches coincide, whatever the value of x , y and $1-x-y$ may be.

In all such cases the equations (1) and (2) may be simplified as follows:

$$\frac{x_2}{1-x_2-y_2} = \frac{x_1}{1-x_1-y_1} e^{\mu'_{x_1}}$$

and

$$\frac{y_2}{1-x_2-y_2} = \frac{y_1}{1-x_1-y_1} e^{\mu'_{y_1}}$$

If the pressure increases μ'_x and μ'_y begin to differ from zero, and properly speaking these quantities always differ from zero. This is to be ascribed to the deviation from the law of BOYLE which occurs in a different degree for different mixtures. But just as we do not commit considerable errors if we neglect the deviation from the law

of BOYLE for rare vapours, but obtain utterly absurd results, if we neglect this deviation for liquids, in the same way we may neglect the difference in the degree of this deviation according to the different composition, if we are treating of a rare vapour phasis, but if we should disregard this difference in the case of a liquid phasis it would lead to absurdities.

Let us now imagine for the different mixtures the pressure to be so far increased, that the double point in fig. 1, p. 450 is reached. Experimentally this can of course not be performed without disturbing the homogeneity, and without condensation of a part of the vapour phasis, which is compressed. But though what we imagine cannot be realised, yet we may put the question, what would happen with the quantity under consideration, if we according to the principle of continuity, should imagine the homogeneity to continue to exist. Then we find the value of μ for the liquid phasis in that double point, and we may write the equation:

$$\mu = \log \frac{p'}{MRT} + 1. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

The pressure p' in this equation is that one, which we have before called coincidence-pressure. As has already been observed this state cannot be realised. Such a liquid, coexisting with such a vapour would be a state of equilibrium; but an unstable one, or one that is metastable. It is however possible by increasing the pressure still more to get in this way a homogeneous liquid which differs only slightly from the one under consideration and which in fact can be realised as a homogeneous phasis. It appears from fig. (1) that μ for this more compressed liquid is somewhat greater than the value written down in the last equation. But again that surplus of the amount of μ may be neglected. For we have always:

$$MRT d\mu = v dp.$$

But if we calculate the surplus of μ , v represents the liquid-volume. And unless the increase of the pressure should be excessive $\frac{v dp}{MRT}$ is a quantity without significance, if v is a volume of a liquid. From this follows that the quantity which we have represented by μ'_{x_1} may be found approximately in differentiating the above equation (4) and therefore may be represented by:

$$\mu'_{x_1} = \frac{1}{p'} \frac{dp'}{dx_1}.$$

In the same way we have:

$$\mu'_{y_1} = \frac{1}{p'} \frac{dp'}{dy_1},$$

so the dependence of μ'_{x_1} and μ'_{y_1} on the coordinates x_1 and y_1 is reduced to the dependence of the coincidence-pressure on x_1 and y_1 . The coincidence-pressures would be the maximum-pressures of the different mixtures, if they behaved like simple substances. The following relation exists for the coincidence pressures, at least approximately:

$$-\log \frac{p'}{p_{cr}} = f \frac{T_{cr} - T}{T}.$$

Consequently we find:

$$\mu'_{x_1} = - \frac{f}{T} \frac{dT_{cr}}{dx_1} + \frac{d \log p_{cr}}{dx_1}$$

and
$$\mu'_{y_1} = - \frac{f}{T} \frac{dT_{cr}}{dy_1} + \frac{d \log p_{cr}}{dy_1}$$

or
$$\mu'_{x_1} = -f \frac{T_{cr}}{T} \frac{d \log T_{cr}}{dx_1} + \frac{d \log p_{cr}}{dx_1} \quad . \quad . \quad . \quad . \quad . \quad (5)$$

and
$$\mu'_{y_1} = -f \frac{T_{cr}}{T} \frac{d \log T_{cr}}{dy_1} + \frac{d \log p_{cr}}{dy_1} \quad . \quad . \quad . \quad . \quad . \quad (6)$$

It is clear from the deduction that these formulae may only be considered as an approximation for the case, that the vapour-pressure is low, and therefore T much lower than T_{cr} . Putting $f=7$ we may put the factor of the first term at a value of about 12 or 14, and the factor of the second term is unity. If therefore the values of $\frac{d \log T_{cr}}{dx_1}$ and $\frac{d \log T_{cr}}{dy_1}$ have moderate ratios to those of $\frac{d \log p_{cr}}{dx_1}$ and $\frac{d \log p_{cr}}{dy_1}$ we find for μ a course not differing much from proportionality to $-\frac{dT_{cr}}{dx_1}$. So we obtain a result in a way, totally differing from that in which I had obtained it before (Cont. II, p. 148 etc.) But in the way we have now followed we are enabled to add a correction term. Of course these equations (5) and (6) are only approximations, and that, for several reasons. But we must distinguish between the character of these approximations. In the first place we have assumed that μ'_{x_2} and μ'_{y_2} vanish for a vapour phasis, and so that μ for different mixtures at the same pressure has the same value. If the density of the vapour phases is so small, that they do not perceptibly deviate from the laws of BOYLE and GAY-LUSSAC everyone will agree that this approximation may be admitted. In the second place we have ascribed to μ for the liquid

state the value which it has in the double-point, though the pressure exceeds that of the double-point. This approximation comes to the same as to say that we neglect the volume of the liquid compared with that of the vapour; and also this approximation is of no signification if the gases are very rare. But the chief reason, for which we have to consider these equations (4) and (5) only as approximations is that we make use of the following relation for the pressure of the double-point :

$$-\log \frac{p'}{p_{cr}} = f \left(\frac{T_{cr}}{T} - 1 \right)$$

if we suppose in this equation f for all substances and so also for all mixtures to be the same and independent of the temperature. Therefore if we set :

$$\mu'_{x_1} = \frac{1}{p'} \frac{dp'}{dx_1},$$

we assume a relation, which is incontestable in all those cases, in which the vapour-phasis may be considered as a perfect gas. But if we do more and if we assume a peculiar property of the equation of state, as that one assumed in the formula for the pressure p' of the double-point, the decision of the question, whether the equations (5) and (6) are contestable or not depends upon the question whether the relation used is accurate. Therefore in applying the equations (5) and (6) it is not our aim to obtain numerically perfectly reliable results, but only to get an idea of the course of the coexistence pressure for different mixtures which is in the main reliable, and which makes us understand the phenomena.

According to these considerations, knowledge of the pressure of the double-points is required for the determination of the shape of the surface of saturation. If we introduce this pressure also into the graphical representation, we add a third surface to the two surfaces, liquid sheet and vapour sheet. The third sheet is found between the first and the second one, and the only points which it has in common with them are those above the angles of the rightangled triangle. In the case, that points of maximum pressure occur, in which points the liquid sheet and the vapour sheet touch each other, this third sheet also will touch both of them. If we cut these three sheets by a plane $p = C$, we get three sections and the projections of these sections are the curves, which we have already mentioned in (a) p. 3 as curves of equal pressure; to these however is added the curve of equal coincidence pressure. After this expatiation on the signification of the quantities occurring in formula II, p. 3, we

will return to the question if we can determine the shape of these projections. In these calculations we confine ourselves to the case of small vapour pressure.

We may put (see p. 7):

$$\frac{x_2}{1-x_2-y_2} = \frac{x_1}{1-x_1-y_1} e^{\mu' x_1}$$

and

$$\frac{y_2}{1-x_2-y_2} = \frac{y_1}{1-x_1-y_1} e^{\mu' y_1}$$

Adding these equations we get:

$$-1 + \frac{1}{1-x_2-y_2} = \frac{x_1 e^{\mu' x_1} + y_1 e^{\mu' y_1}}{1-x_1-y_1}$$

or

$$\frac{1}{1-x_2-y_2} = \frac{1+x_1(e^{\mu' x_1}-1)+y_1(e^{\mu' y_1}-1)}{1-x_1-y_1}$$

Hence also:

$$\frac{x_2}{x_1} = \frac{e^{\mu' x_1}}{1+x_1(e^{\mu' x_1}-1)+y_1(e^{\mu' y_1}-1)}$$

and

$$\frac{y_2}{y_1} = \frac{e^{\mu' y_1}}{1+x_1(e^{\mu' x_1}-1)+y_1(e^{\mu' y_1}-1)}$$

In the same way:
$$\frac{x_2-x_1}{x_1} = \frac{(1-x_1)(e^{\mu' x_1}-1)-y_1(e^{\mu' y_1}-1)}{1+x_1(e^{\mu' x_1}-1)+y_1(e^{\mu' y_1}-1)}$$

and

$$\frac{y_2-y_1}{y_1} = \frac{(1-y_1)(e^{\mu' y_1}-1)-x_1(e^{\mu' x_1}-1)}{1+x_1(e^{\mu' x_1}-1)+y_1(e^{\mu' y_1}-1)}$$

If we substitute in equation II these values of x_2-x_1 and of y_2-y_1 , and the values of $\frac{\partial^2 \zeta}{\partial x_1^2}$, $\frac{\partial^2 \zeta}{\partial x_1 \partial y_1}$ and $\frac{\partial^2 \zeta}{\partial y_1^2}$ found on page 5 and if we divide by MRT then we find the following differential equations, where we denote for brevity's sake by N the nominator of the fractions indicating the values of x_2-x_1 , and y_2-y_1 ,

$$\begin{aligned} 0 = & \frac{(1-x_1)(e^{\mu' x_1}-1)-y_1(e^{\mu' y_1}-1)}{N} \left\{ \frac{1-y_1}{1-x_1-y_1} + x_1 \mu''_{x_1} \right\} dx_1 + \\ & + \frac{(1-y_1)(e^{\mu' y_1}-1)-x_1(e^{\mu' x_1}-1)}{N} \left\{ \frac{y_1}{x_1-y_1} + y_1 \mu''_{x_1 y_1} \right\} dx_1 + \\ & + \frac{(1-x_1)(e^{\mu' x_1}-1)-y_1(e^{\mu' y_1}-1)}{N} \left\{ \frac{x_1}{1-x_1-y_1} + x_1 \mu''_{x_1 y_1} \right\} dy_1 + \\ & + \frac{(1-y_1)(e^{\mu' y_1}-1)-x_1(e^{\mu' x_1}-1)}{N} \left\{ \frac{1-x_1}{1-x_1-y_1} + y_1 \mu''_{y_1} \right\} dy_1. \end{aligned}$$

If we put: $\mu''_{x_1} dx_1 + \mu''_{x_1 y_1} dy_1 = d\mu'_{x_1}$ and $\mu''_{x_1 y_1} dx_1 + \mu''_{y_1} dy_1 = d\mu'_{y_1}$, then we may write this equation in the following form:

$$0 = d \log \{1 + x_1 (e^{\mu'_{x_1}} - 1) + y_1 (e^{\mu'_{y_1}} - 1)\} - x_1 d\mu'_{x_1} - y_1 d\mu'_{y_1}$$

$$\text{or } C = \log \{1 + x_1 (e^{\mu'_{x_1}} - 1) + y_1 (e^{\mu'_{y_1}} - 1)\} + \mu_{x_1 y_1} - x_1 \mu'_{x_1} - y_1 \mu'_{y_1}$$

Applying equation (3) of p. 5 it would have been possible to obtain this integral for the projection of the curves of equal pressure in a simpler way. In this equation, where the index 2 indicates again a rare vapour phasis, we equate μ'_{x_2} and μ'_{y_2} to zero and μ_2 to

$\log \frac{p}{MRT} + 1$; so we get:

$$\log (1 - x_1 - y_1) + \mu_{x_1 y_1} - x_1 \mu'_{x_1} - y_1 \mu'_{y_1} = \log (1 - x_2 - y_2) + \log \frac{p}{MRT} + 1,$$

from which follows:

$$\log \frac{p}{MRT} = \log \frac{1 - x_1 - y_1}{1 - x_2 - y_2} + \mu_{x_1 y_1} - x_1 \mu'_{x_1} - y_1 \mu'_{y_1} - 1$$

In connection with the value I have given before

$$\log \frac{p}{MRT} = \frac{1 - x_1 - y_1}{1 - x_2 - y_2} = 1 + x_1 (e^{\mu'_{x_1}} - 1) + y_1 (e^{\mu'_{y_1}} - 1)$$

This equation may be written in the following form:

$$\log \frac{p}{MRT} = \log \{1 + x_1 (e^{\mu'_{x_1}} - 1) + y_1 (e^{\mu'_{y_1}} - 1)\} + \mu_{x_1 y_1} - x_1 \mu'_{x_1} - y_1 \mu'_{y_1} - 1. \quad (7)$$

Already long ago I have given a corresponding equation for a binary system. It may also be found Cont. II, p. 146, though in a somewhat modified form. I have shown for the case of a binary mixture, that such an equation in some cases may represent a straight line, but that it in other cases represents a curve, which at certain values of x_1 presents a maximum value for p . The intermediate forms may also occur of course. The course of the function μ being at least approximately determined by that of the functions T_c and p_{cr} , knowledge of the dependence of these functions on x and y would be required for an adequate discussion of equation (7). This would be possible according to my equation of state putting

$$T_{cr} = \frac{8}{27} \frac{a}{b} \quad \text{and} \quad p_{cr} = \frac{1}{27} \frac{a}{b^2}.$$

But as the quantities $\frac{a}{b}$ and $\frac{a}{b^2}$ depend rather intricately on x and y this would lead to an elaborate discussion, and I have not yet suc

ceeded in drawing simple conclusions from it in a concise manner and to formulate them sharply. In the formula

$$\mu = -f\left(\frac{T_{cr}}{T}-1\right) + \log p_{cr}$$

the discussion of the term T_{cr} and of its first and second derivative function according to x and y would already require extensive calculations, and the discussion of $\log p_{cr}$ and its derivatives would still augment the difficulties considerably. And though it is true, as we have observed above, that generally the influence of $\log p_{cr}$ is not great, yet some cases occur, namely those, in which $\frac{dT_{cr}}{dx}$ and $\frac{dT_{cr}}{dy}$ are small, in which this influence is decisive. Therefore for the present I will not enter into an accurate discussion, and only investigate some peculiar cases.

So as first case we may suppose that the three components have been chosen in such a way, that the course of p will be represented by a straight line for each of the three pairs, which may be formed from the components of the ternary system. This may be the case if the difference of the critical temperatures of the components of these pairs is considerable and the critical pressures either differ but slightly or have such values that the expression:

$$-f\frac{dT_{cr}}{Tdx} + \frac{dp_{cr}}{p_{cr}dx}$$

may be considered to be constant for each of the three pairs. Then we may expect that for the ternary system μ'_{x_1} and μ'_{y_1} will be everywhere constant or nearly constant, from which follows that $d\mu'_{x_1}$ and $d\mu'_{y_1}$ may be neglected compared with μ'_{x_1} and μ'_{y_1} . If we in fact neglect the values of $d\mu'_{x_1}$ and $d\mu'_{y_1}$ the differential equation of the curves of equal pressure assumes the following form:

$$0 = d \log \{1 + x_1 (e^{\mu'_{x_1}} - 1) + y_1 (e^{\mu'_{y_1}} - 1)\}.$$

And we get for the equation of the projection of these curves:

$$C = 1 + x_1 (e^{\mu'_{x_1}} - 1) + y_1 (e^{\mu'_{y_1}} - 1).$$

And we find for the value of p from equation (7)

$$p = MRT e^{\mu_0 - 1} \{1 + x_1 (e^{\mu'_{x_1}} - 1) + y_1 (e^{\mu'_{y_1}} - 1)\}.$$

The supposition namely that $d\mu'_{x_1}$ and $d\mu'_{y_1}$ are zero comes to the

same as to take two different constants for μ'_{x_1} and μ'_{y_1} . But then we have also:

$$\mu_{x_1 y_1} = \mu_0 + x_1 c_1 + y_1 c_2,$$

where μ_0 denotes the value of $\mu_{x_1 y_1}$ for the first component.

From this we deduce that the liquid sheet of the saturation surface is a plane, and so that:

$$p = p_1 (1 - x_1 - y_1) + p_2 x_1 + p_3 y_1 \quad . \quad . \quad . \quad . \quad . \quad (8)$$

We deduce this form for p by making use of the relations for each of the components:

$$p_1 = MRT e^{\mu_0 - 1}$$

$$p_2 = MRT e^{\mu_0 + \mu'_{x_1} - 1}$$

$$p_3 = MRT e^{\mu_0 + \mu'_{y_1} - 1}$$

The value $e^{\mu'_{x_1}}$ which is constant in this case, is equal to $\frac{p_2}{p_1}$ and

the value of $e^{\mu'_{y_1}}$ is equal to $\frac{p_3}{p_1}$.

The lines of equal pressure for liquids are therefore all parallel to each other. If $p = p_2$ the projection of such a line is:

$$1 - x - \frac{p_3 - p_1}{p_2 - p_1} y = 0$$

It cuts therefore the Y -axis at the point $y = \frac{p_2 - p_1}{p_3 - p_1}$. It appears that in this case we have the interesting circumstance, that the addition of a substance with a given maximum tension to a binary mixture whose vapour pressure is equal to that maximum tension, does not bring about any variation of that pressure, however great or small the added quantity may be.

The other line of equal pressure, the section of the vapour sheet, lying at the same height of p , and representing phases coexisting with those of the first line, may be deduced from:

$$p = p_1 (1 - x_1 - y_1) + p_2 x_1 + p_3 y_1$$

if we express in this equation x_1 and y_1 in x_2 and y_2 ; and this may be easily done if μ'_{x_2} and μ'_{y_2} vanish, and μ'_{x_1} and μ'_{y_1} may be considered as constants. We write then:

$$\frac{x_1}{1 - x_1 - y_1} = \frac{x_2}{1 - x_2 - y_2} e^{-\mu'_{x_1}}$$

and

$$\frac{y_1}{1 - x_1 - y_1} = \frac{y_2}{1 - x_2 - y_2} e^{-\mu'_{y_1}}$$

These equations would also hold, if μ'_{x_1} and μ'_{y_1} still depended on x_1 and y_1 , but then it would not be possible to express x_1 and y_1 in x_2 and y_2 . Performing the substitutions mentioned we get:

$$\frac{1}{p} = \frac{1-x_2-y_2}{p_1} + \frac{x_2}{p_2} + \frac{y_2}{p_3} \dots \dots \dots (9)$$

As it is however not only our aim to obtain the results, but as we also wish to interpret the equations given before, we return to equation II in order to determine the line of equal pressure for the vapour phases.

If we continue to use the index 2 for the vapour phasis, and the index 1 for the liquid phasis, but if we now apply equation II to the vapour phases, it assumes the following form:

$$v_{12} dp = \left\{ (x_1-x_2) \frac{\partial^2 \zeta}{\partial x_2^2} + (y_1-y_2) \frac{\partial^2 \zeta}{\partial x_2 \partial y_2} \right\} dx_2 + \\ + \left\{ (x_1-x_2) \frac{\partial^2 \zeta}{\partial x_2 \partial y_2} + (y_1-y_2) \frac{\partial^2 \zeta}{\partial y_2^2} \right\} dy_2.$$

As we may neglect μ'_{x_2} and μ'_{y_2} for the vapour phases, we may also neglect the second derivatives of μ ; and we may put:

$$\frac{\partial^2 \zeta}{\partial x_2^2} = MRT \frac{1-y_2}{x_2(1-x_2-y_2)}, \quad \frac{\partial^2 \zeta}{\partial x_2 \partial y_2} = MRT \frac{1}{1-x_2-y_2}$$

and
$$\frac{\partial^2 \zeta}{\partial y_2^2} = MRT \frac{1-x_2}{y_2(1-x_2-y_2)}.$$

We have $v_{12} = v_1 - v_2 - (x_1 - x_2) \left(\frac{dv}{dx_2} \right)_p - (y_1 - y_2) \left(\frac{dv}{dy_2} \right)_p$; and $\left(\frac{dv}{dx_2} \right)_p$ and $\left(\frac{dv}{dy_2} \right)_p$ are zero for the vapour which we assume to follow the law of Boyle, and so to occupy the same volume, if the pressure and the number of molecules are constant. If we neglect moreover the volume v_1 of the liquid compared with v_2 the volume of the vapour, then we get after division by MRT :

$$-\frac{dp}{p} = \left\{ (x_1-x_2) \frac{1-y_2}{v_2(1-x_2-y_2)} + \frac{y_1-y_2}{1-x_2-y_2} \right\} dx_2 + \\ + \left\{ \frac{x_1-x_2}{1-x_2-y_2} + (y_1-y_2) \frac{1-x_2}{y_2(1-x_2-y_2)} \right\} dy_2.$$

For a binary system this yields the well known equation:

$$\frac{dp}{p} = \frac{x_2-x_1}{x_2(1-x_2)} dx_2.$$

If further we substitute for x_1-x_2 and y_1-y_2 the values :

$$x_1-x_2 = x_2 \frac{(1-x_2)(e^{-\mu'x_1}-1)-y_2(e^{-\mu'y_1}-1)}{(1-x_2-y_2)+x_2e^{-\mu'x_1}+y_2e^{-\mu'y_1}}$$

and
$$y_1-y_2 = y_2 \frac{(1-y_2)(e^{-\mu'y_1}-1)-x_2(e^{-\mu'x_1}-1)}{(1-x_2-y_2)+x_2e^{-\mu'x_1}+y_2e^{-\mu'y_1}},$$

then we get by integration :

$$p = \frac{C}{(1-x_2-y_2)+x_2e^{-\mu'x_1}+y_2e^{-\mu'y_1}},$$

or in connection with the value of $e^{-\mu'x_1}$ and $e^{-\mu'y_1}$ given before :

$$p = \frac{C}{(1-x_2-y_2)+x_2\frac{p_1}{p_2}+y_2\frac{p_1}{p_3}}$$

The constant C is of course the pressure for the case that x_2 and y_2 are equal to zero, so it is equal to p_1 , and we find again equation (9). If we now give to p the same value as for the liquid sheet, we find the second branch of the curve of equal pressure. So we find for $p = p_2$:

$$1-x_2 = \frac{p_2}{p_3} \frac{p_3-p_1}{p_2-p_1} y_2,$$

a line which yields $y_2 = 1$ for $x_2 = 0$ and :

$$y_2 = \frac{p_3}{p_2} \frac{p_2-p_1}{p_3-p_1}$$

for the point of intersection with the axis for the third component. This value is of course the value of y_2 for the pressure p_2 of the vapour phasis of the binary system consisting of the first and the third component. The projections of these vapour lines of equal pressure are again parallel.

The line :

$$\frac{1}{p} - \frac{1}{p_1} = x_2 \left(\frac{1}{p_2} - \frac{1}{p_1} \right) + y_2 \left(\frac{1}{p_3} - \frac{1}{p_1} \right)$$

is displaced parallel to itself, when the value of p varies. The vapour sheet consists therefore of parallel lines and may be considered as a cylindrical surface. The section with the POX plane is a hyperbola, and also that with the POY plane.

If we cut the sheet of the coincidence pressures also at the same

height, we get a third line, which lies between the two former ones, and which we have already mentioned in our first communication as the projection of the line of the double-points. The equation of this line may be found from the equations of p. 8 and 9 namely from:

$$\frac{1}{p'} \frac{dp'}{dx} = \mu'_{x_1}$$

and

$$\frac{1}{p'} \frac{dp'}{dy} = \mu'_{y_1}.$$

In this case we have $\mu'_{x_1} = \log \frac{p_2}{p_1}$ and $\mu'_{y_1} = \log \frac{p_3}{p_1}$; integrating we find for the equation of this curve:

$$\log p' = c + x \log \frac{p_2}{p_1} + y \log \frac{p_3}{p_1}.$$

If x and $y = 0$, this third sheet coincides with the two others, and $p' = p_1$; from this the value of C may be calculated. We may also write this equation in the following form:

$$p' = p_1^{(1-x-y)} p_2^x p_3^y$$

or
$$\log p' = (1-x-y) \log p_1 + x \log p_2 + y \log p_3.$$

This equation also represents a right line, which is displaced parallel to itself, if p' varies.

So we find very simple lines for the three curves, which we get in this case for a binary system, namely a right line, a hyperbola, and between them an exponential curve.

We shall now discuss the case which differs most from that which we have treated, namely that, in which each of the pairs that may be formed from the components of the ternary system, presents a maximum pressure. The critical temperatures of the components do not differ much in this case, and for each pair a composition may be found, for which the function μ' vanishes. Then we may expect, that for the ternary system a value for x_1 and for y_1 may be found for which the values of μ'_{x_1} and μ'_{y_1} are equal to zero. If the function μ' depended only on T_{cr} , then we might simply express this in properties of T_{cr} , and we might say: for each of the pairs a minimum critical temperature occurs, so we may also expect a minimum value for T_{cr} for the ternary system. As μ still contains the term $\log p_{cr}$, the same set of values of x_1 and y_1 which yields the minimum value of T_{cr} will not make μ'_{x_1} and μ'_{y_1} vanish. This agrees indeed with the considerations for a binary mixture, given in Cont. II.

For values of x_1 and y_1 differing only slightly from those, for which

μ'_{x_1} and μ'_{y_1} vanish, the first derivatives of μ may be considered to be small in this case but the second derivatives on the other hand will be decisive for the course.

In order to determine for this case also the projection of the curves of constant pressure we will make use of equation (7):

$$\log \frac{p}{p_m} = \log \{1 + x_1(e^{\mu'_{x_1}} - 1) + y_1(e^{\mu'_{y_1}} - 1)\} + \mu_{x_1 y_1} - x_1 \mu'_{x_1} - y_1 \mu'_{y_1} - 1.$$

If we call the values of x_1 and y_1 , for which μ'_{x_1} and μ'_{y_1} vanish, x_m and y_m and the corresponding pressure p_m , then we have:

$$\log \frac{p_m}{MRT} = \mu_m - 1 \quad \text{hence also:}$$

$$\log \frac{p}{p_m} = \log \{1 + x_1(e^{\mu'_{x_1}} - 1) + y_1(e^{\mu'_{y_1}} - 1)\} + \mu_{x_1 y_1} - x_1 \mu'_{x_1} - y_1 \mu'_{y_1} - \mu_m.$$

It appears already from this form of p_m that this pressure of this system may be considered as a coincidence pressure, and as this system can be realised, it may be considered as an ordinary maximum tension. If we now consider μ'_{x_1} and μ'_{y_1} to be small, so that

$$\text{we may put } e^{\mu'_{x_1}} - 1 = \mu'_{x_1} \text{ and } e^{\mu'_{y_1}} - 1 = \mu'_{y_1} \text{ and}$$

$$\log \{1 + x_1 \mu'_{x_1} + y_1 \mu'_{y_1}\} = x_1 \mu'_{x_1} + y_1 \mu'_{y_1},$$

then we find for mixtures, whose composition does not differ much from x_m and y_m :

$$\log \frac{p}{p_m} = \mu_{x_1 y_1} - \mu_m.$$

If we write:

$$\mu_{x_1 y_1} = \mu_m + \frac{1}{2} \{(x_1 - x_m)^2 \mu''_{x_m} + 2(x_1 - x_m)(y_1 - y_m) \mu''_{x_m y_m} + (y_1 - y_m)^2 \mu''_{y_m}\} -$$

we may write the last equation:

$$\log \frac{p}{p_m} = \frac{1}{2} \{(x_1 - x_m)^2 \mu''_{x_m} + 2(x_1 - x_m)(y_1 - y_m) \mu''_{x_m y_m} + (y_1 - y_m)^2 \mu''_{y_m}\}.$$

If we only inquire into the mathematical consequences of this last equation, without trying to answer the question, if the suppositions as to the values, which we have ascribed to μ''_{x_m} , $\mu''_{x_m y_m}$ and μ''_{y_m} , may be found in nature, we may only say, that if μ'_{x_m} and μ'_{y_m} vanish, the curves of equal pressure in the immediate neighbourhood of this singular point will be conic sections. In order that p_m may be really a maximum pressure, the first member must be negative for all real values of $x_1 - x_m$ and $y_1 - y_m$ and this requires, that μ''_{x_m} and μ''_{y_m} are both negative and that $(\mu''_{x_m y_m})^2 < \mu''_{x_m} \mu''_{y_m}$. Then the curves of equal pressure are ellipses whose centre is the singular point. For a binary mixture the quantity μ''_x has always appeared to be negative in accordance with this theory, when the components were

substances, which do not exercise any chemical action upon one another, for which therefore the molecules in the mixture may be considered to be simply mixed, without suffering any internal modification. For such binary mixtures minimum critical temperatures have actually been found, — and the chief term of μ being $—f\left(\frac{T_{cr}}{T} - 1\right)$

a minimum value of T_{cr} corresponds to a negative value of μ''_{x_3} — but never with certainty maximum critical temperatures. If μ''_{x_m} and μ''_{y_m} could be positive, and $\mu''_{x_m}\mu''_{y_m} > (\mu''_{xmy_m})^2$, then we should also get ellipses for the curves of equal pressure, but then we should have $p > p_m$, and the ternary system would present a minimum pressure, which would also lead to minimum pressures for the pairs of which the system consists. If maximum critical temperature for a binary system should really occur in nature, and if we then formed a ternary system, of which one pair of components presented a maximum and another pair a minimum value of T_{cr} , then μ''_{x_m} and μ''_{y_m} might have opposite signs, and the point for which μ'_{x_m} and μ'_{y_m} vanish would be a stationary point as to the pressure, and the curves of equal pressure would intersect in that point.

In figure 12 the course of the curves of equal pressure has been represented schematically for the case of maximum pressure for the three pairs of components and for maximum pressure for a point of the system. The succession of the values of the pressure is then :

Fig. 12.

$$p_1 < p_2 < p_{12} < p_3 < p_{13} < p_{23} < p_m,$$

only the order of succession of p_{12} and p_3 and of p_{13} and p_{23} may be reversed. The figure does not require any further explanation.

As intermediate case for the course of the curves of equal pressure, we assume a system, in which for two of the pairs the pressure increases or decreases regularly, but the third pair has a maximum pressure. So in fig. 13 the pressures follow each other in this way : $p_1 < p_2 < p_{12} < p_3$. One of the

curves of equal pressure, namely that one for which $p = p_{12}$, touches the OX -axis.

In the following chapter we will give some indications concerning the course of the curves of constant pressure for the vapour phases in this case, and in the general case. Let us return to that purpose to equation II of p. 3 of this communication.

b. Displacement of the curves of equal pressure with variation of the pressure.

We have already observed that the projection of the connodal curve of a ξ -surface, construed for a certain value of p coincides with the projection of the curves, for which the pressure is equal to p , and that therefore all laws, which hold for the connodal curve, also apply to the curves of equal pressure.

If in the equation:

$$v_{21} dp = \left\{ (x_2 - x_1) \frac{\partial^2 \xi}{\partial x_1^2} + (y_2 - y_1) \frac{\partial^2 \xi}{\partial x_1 \partial y_1} \right\} dx_1 + \\ + \left\{ (x_2 - x_1) \frac{\partial^2 \xi}{\partial x_1 \partial y_1} + (y_2 - y_1) \frac{\partial^2 \xi}{\partial y_1^2} \right\} dy_1$$

we choose the values of dx_1 and dy_1 such, that

$$\frac{dx_1}{x_2 - x_1} = \frac{dy_1}{y_2 - y_1} = \frac{dl}{L}$$

where L represents the length of a line, connecting the point P_1 , whose coordinates are x_1 and y_1 with the point P_2 , representing the phasis coexisting with P_1 and whose coordinates are x_2 and y_2 . Be further dl the length of a line, whose projections are dx_1 and dy_1 , then the point $x_1 + dx_1, y_1 + dy_1$ lies between the points P_1 and P_2 . It lies therefore in what we may call the heterogeneous region. The above equation may then be written:

$$v_{21} \frac{dp}{dl} = L \left\{ \frac{\partial^2 \xi}{\partial x_1^2} \left(\frac{dx_1}{dl} \right)^2 + 2 \frac{\partial^2 \xi}{\partial x_1 \partial y_1} \left(\frac{dx_1}{dl} \right) \left(\frac{dy_1}{dl} \right) + \frac{\partial^2 \xi}{\partial y_1^2} \left(\frac{dy_1}{dl} \right)^2 \right\}.$$

The second member of this equation is positive for the points of the connodal curve, as the ξ -surface lies above the tangent plane for all phases which may be realised. If the point P_1 represents a liquid phasis, then v_{21} is positive, and therefore $\frac{dp}{dl}$ also positive.

When the pressure increases the liquid branch is displaced in such a way, that it moves towards the side of what was before the heterogeneous region. This rule for a ternary system is equivalent

to the rule of KONOWALOW for a binary system, if this latter rule is duly extended. If on the other hand P_1 lies on the liquid sheet, then v_{21} and therefore also $\frac{dp}{dl}$ is negative. This signifies that the vapour branch of the curves of equal pressure moves on towards the heterogeneous region if the pressure *decreases*, and on the other hand towards the region which at constant pressure belonged to the homogeneous region, if the temperature *increases*. If the pressure is varied the two branches move, in such a way, that one of the branches retreats for the other. If there is not yet question of critical phenomena, a point for which $v_{21} = 0$ does not yet exist, and the given rule holds without exceptions. For the case that no maximum pressure exists, the two branches of the projection of the curves of equal pressure consist of two curves, originating both in the same side of the rightangled triangle, and ending again in the same side. Every point on one of the branches has a conjugated point on the other branch. We will call the lines joining such a pair of conjugated points (coexisting phases) *chords*. The first of these chords have the direction of one of the sides of the rightangled triangle and the last the direction of the other side. If these two sides are the sides containing the right angle, then the chord turns over an angle of 90° . It occurs however only as an exception that the chord is directed towards the origin in other points than the extremities. Afterwards we will return to this question.

If a maximum pressure exists, the branches of the curves of equal pressure form closed curves near the phasis, whose pressure is maximum. The liquid branch contracts if the pressure increases, and according to the rule, deduced above, it moves towards the branch of the vapour phases. This branch therefore must also form a closed curve round the point of maximum pressure and that a smaller one. For the limiting case, the curve for the liquid phases is an ellipse the curve for the vapour phases is also closed, but has other dimensions, and its axes have other directions and another ratio, in the limiting case, however, it must coincide with the ellipse of the liquid phases. At any rate therefore, the position of the liquid branches being given for increasing pressure we may immediately conclude to the relative position of the vapour branches.

(To be continued.)

Physics. — "*Statistical Electro-mechanics.*" By Dr. J. D. VAN DER WAALS Jr. (Communicated by Prof. VAN DER WAALS).

Prof. GIBBS has newly published a treatise entitled "*Elementary principles in statistical mechanics*", in which he communicates some considerations, belonging to a science, which he calls "*Statistical mechanics*," and of which he states that "*on account of the elegance and simplicity of its principles*" it is eminently worthy that the laws to which it is subjected, are studied. The laws relate to the behaviour of a great number of systems, whose motions are mutually independent. These systems quite agree with one another as to their nature, and only differ in so far, that the integration constants of the differential equations of motion have different values, or, what comes to the same, that the values of the generalized coördinates and of the generalized velocities at an arbitrary moment (e. g. at the moment $t = 0$) differ for different systems. The laws, which hold for such ensembles of systems have a very general character, as GIBBS shows; yet in their application they are confined to systems, consisting exclusively of ordinary matter. Now the question arises whether such like considerations might be applied to electro-magnetic systems, and whether in doing so we might extend our very limited knowledge of the phenomena of radiation in connection with the laws of thermodynamics.

We cannot deny however that we must not expect *too much* from these considerations. The greater part of the theses deduced by GIBBS are exclusively or principally applicable to ensembles of systems which he calls canonical and which have such an important place in his considerations, because they represent the simplest law possible of the distribution of the systems over the different "*phases*" ¹⁾. Mathematical simplicity, however, is not a trustworthy criterion, when we want to investigate, what is actually to be found in nature. For our mathematical representation e. g. the simplest motion, a vibrating string can perform, is an harmonic motion, yet we should be utterly mistaken if we should assume, that every vibrating string would execute such a motion. Perhaps we run the risk of making similar mistakes if we assume, that all systems in nature will follow the laws which we have deduced on the supposition of a canonical distribution of the systems of an ensemble.

It is true that GIBBS shows in his chapters XI—XIII that the cano-

¹⁾ Two systems are considered to be in the same phase when they are to be found in the same element of extension in phase.

nical distribution is the most probable one, provided the only condition, to which the ensemble is subjected, be that the mean value of the energy of the systems is a prescribed quantity; but the main difficulty happens to be to answer the question whether this is indeed the only condition. Systems e. g., consisting of spherical, mutually equal molecules, will not be distributed canonically, for they are still subjected to another condition, namely the distance of two centres of molecules can never be less than the diameter. To assume the canonical distribution comes therefore to the same as to neglect the volume of the molecules, but it is not easy to decide whether nothing else is neglected. In fact choosing the distribution of the systems of an ensemble is equivalent to choosing the cases, which we are to consider as "cases of equal probability" in a more direct application of the calculus of probabilities. Both are subject to the chance, that the probability a posteriori will prove to be another than we had assumed a priori.

Yet such like considerations can be useful, in the *known* region of thermodynamics, because they bring its laws very simply and elegantly together under one point of view; in the yet *unknown* region, because they may perhaps suggest formulae, for which comparison with the experiments may decide, whether they are in accordance with the phenomena of nature or not.

Law of conservation of density-in-phase.

In an investigation, whether the considerations of GIBBS are also applicable for electro-magnetic systems, we have in the first place to examine, whether the "law of conservation of density-in-phase" holds also for them. In the beginning we will confine ourselves to systems devoid of material, electrical or magnetical masses.

Now we imagine an ensemble of systems. The different systems are congruent spaces, enclosed by perfectly reflecting walls. We divide each system into n equal cubic elements of space $dx\ dy\ dz$. These elements are so small that the electric and magnetic forces in them may be considered to be constant. The state of each system will be perfectly defined, if in each element of space the components f , g and h of the electric displacement, and the components α , β and γ of the magnetic induction are given. So the state is determined by means of $6\ n$ data; according to the assumption, that electric energy is potential, magnetic energy kinetic, the $3\ n$ components of the electric displacement would represent coordinates, the $3\ n$ components of magnetic induction generalized momenta, or at least they would be proportional to them.

We mark the elements of space with successive numbers and represent the components of the vectors in the r^{th} element by $f_r, g_r, h_r, \alpha_r, \beta_r$ and γ_r . Let us select from an ensemble those systems whose data lie between the limits f_1 and $f_1 + df_1, f_2$ and $f_2 + df_2 \dots f_n$ and $f_n + df_n$ and in the same way for the other components; the number of these systems may be represented by:

$$D df_1 \dots df_n dg_1 \dots dg_n dh_1 \dots dh_n d\alpha_1 \dots d\alpha_n d\beta_1 \dots d\beta_n d\gamma_1 \dots d\gamma_n$$

or

$$D [(df_1)] [(d\alpha_1)] \dots \dots \dots (1)$$

Here the brackets indicate, that also the other components, the parentheses that the same quantities also for the other elements of space are to be taken. We will call $[(df_1)] [(d\alpha_1)]$ an element of extension-in-phase, D the density-in-phase, $P = \frac{D}{N}$ the coefficient of probability-in-phase (N representing the total number of systems in the ensemble) and η , defined by the equation $P = e^\eta$, the index of probability-in-phase.

Let us consider the same ensemble after a short lapse of time dt , then the number of systems being in a certain phase, will have varied. We may conceive the variation of that number to be composed of $12n$ parts, as the systems may enter or leave a certain phase by passing one of $12n$ different limits, $[(f_1)], [(f_1 + df_1)], [(a_1)]$ and $[(a_1 + da_1)]$.

The systems passing the limit f_1 contribute:

$$D \frac{df_1}{dt} dt df_2 \dots df_n dg_1 \dots dg_n dh_1 \dots dh_n [(d\alpha_1)] \dots \dots \dots (2)$$

to the total number with which the quantity $D [(df_1)] [(d\alpha_1)]$ increases.

The systems passing the limit $f_1 + df_1$ contribute a decrease amounting to:

$$\left\{ D \frac{df_1}{dt} + \frac{\partial}{\partial f_1} \left\{ D \frac{df_1}{dt} \right\} df_1 \right\} dt df_2 \dots dh_n [(d\alpha_1)] \dots \dots (3)$$

Adding these quantities we get an increase with:

$$- \frac{\partial}{\partial f_1} \left\{ D \frac{df_1}{dt} \right\} dt [(df_1)] [(d\alpha_1)] \dots \dots \dots (4)$$

Now we have:

$$\frac{\partial}{\partial f_1} \left\{ D \frac{df_1}{dt} \right\} = \frac{\partial D}{\partial f_1} \frac{df_1}{dt} + D \frac{\partial}{\partial f_1} \frac{df_1}{dt} \dots \dots \dots (5)$$

The second term of the second member is zero, for $\frac{df_1}{dt}$ depends only on the rotation of the magnetic induction, and is independent of the value of f_1 .

In the same way we find the increase in consequence of the systems passing the other limits, — taking into account that all quantities of the form $\frac{\partial}{\partial \alpha_1} \frac{d\alpha_1}{dt}$ are zero. — Taking the sum of all these partial increases and dividing by $[(df'_1)] [(d\alpha_1)]$ we find:

$$\frac{\partial D}{\partial t} = - \left[\left(\frac{\partial D}{\partial f'_1} \frac{df'_1}{dt} \right) \right] - \left[\left(\frac{\partial D}{\partial \alpha_1} \frac{d\alpha_1}{dt} \right) \right] \cdot \cdot \cdot \cdot \cdot \quad (6)$$

or:
$$\frac{\partial D}{\partial t} + \left[\left(\frac{\partial D}{\partial f'_1} \frac{df'_1}{dt} \right) \right] + \left[\left(\frac{\partial D}{\partial \alpha_1} \frac{d\alpha_1}{dt} \right) \right] = \frac{dD}{dt} = 0. \cdot \cdot \cdot \quad (7)$$

Here $\frac{\partial D}{\partial t}$ represents the flucton of the density for a phasis whose limits are constant, $\frac{dD}{dt}$ for a phasis whose limits partake of the motion of the systems of the ensemble.

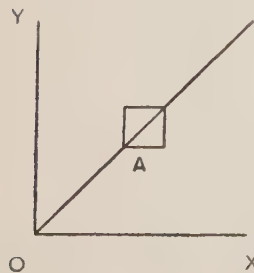
So the density proves to be constant for a phasis, partaking of the motion of the systems, and as, of course, the systems can never pass the limits of an extension-in-phase, when these limits move with the systems, the total number of systems within every extension-in-phase, i. e. $D [(df'_1)] [(d\alpha_1)]$ remains constant, and so also $[(df'_1)] [(d\alpha_1)]$.

This proof of the laws of conservation of density-in-phase and of extension-in-phase quite agrees with that one given by GIBBS. In our case, however, we have still to pay attention to one circumstance.

In calculating $\frac{\partial D}{\partial t} [(df'_1)] [(d\alpha_1)]$, we have assumed, that this number is the sum of the numbers of systems passing the different limits. This comes to the same as to say that no system will pass more than one of the limits during the time dt , or at least, that the number of the systems that pass more than one limit is so small, that it may be neglected. In the proof of GIBBS we may assume, that this is really the case, provided we take dt so small, that $\frac{dq}{dt} dt$ is small

compared with dq (where q represents one of the generalized coordinates, and dq one of the dimensions of an element of extension-in-phase). For our case however this proof is incomplete. Be r and s two adjacent elements of space, then $[f'_r]$ and $[f'_s]$, $[\alpha_r]$ and $[\alpha_s]$ are no independent quantities, but they must be approximately equal, as $[f']$ and $[\alpha]$ vary only fluently from point to point.

In order to investigate the consequences of this circumstance we imagine an ensemble of



systems with only two coordinates x and y , which are subjected to the condition that x and y must be equal and continue to be so. All systems will then be found on the line OA and will move in the direction of this line, so all systems leaving the element of space drawn in the figure, or entering into it, will pass the two limits dx and dy at the same moment. If the condition is not that x and y must be rigorously equal, but only that their difference must be very small, then all systems will be huddled up very near the line OA and a great part of those that pass the limit dx will also pass the limit dy . It is evident, that this circumstance is caused by the fact, that within the element $dx dy$ the density is not homogeneous. If we choose therefore the dimensions dx and dy so small, that the whole element lies within a region, where the density may be considered as constant, then we may again assume that the number of systems, passing both limits may be neglected, compared with the number of systems passing only one of the two limits.

If we choose therefore $[(df_1)]$ and $[(d\alpha_1)]$ small compared with the mean value of $\left[\left(\frac{\partial f_1}{\partial x} dx\right)\right]$ and $\left[\left(\frac{\partial \alpha_1}{\partial x} dx\right)\right]$, so e. g. having a finite ratio to dx^2 , and dt again small compared with the quantities $[(df_1)]$ and $[(d\alpha_1)]$, so e. g. having a finite ratio to dx^3 , it appears that in fact the number of systems passing more than one of the limits may be neglected. So the proof of the law of conservation of density-in-phase is complete.

The quasi-canonical distribution.

If we wish to distribute the systems of an ensemble over the different phases in such a way, that the distribution does not vary with the time, so that the state of the ensemble is stationary, it is evident that we have to choose for P a function of the coordinates, which is constant in time. GIBBS chooses for this purpose the function

$$e^{\psi - \varepsilon}$$

where ε represents the energy of a system, and ψ and θ are constant quantities for a given ensemble. He calls this distribution the canonical distribution. This simple law cannot be applied to systems consisting of ether. If we assumed it, the quantities $[f]$ and $[\alpha]$ would vary abruptly from element to element instead of varying fluently, and moreover the distribution would depend on the dimensions of the elements of space, which we have arbitrarily chosen. We must therefore assume another distribution which secures a fluent variation of the electric and magnetic displacements.

To this purpose we will assume a distribution closely resembling those, discussed by GIBBS in his chapter IV as "other distributions having the same properties as the canonical." These distributions have the characteristic property, that the index of probability η is a linear function of one or more functions F_1, F_2 etc. of the coordinates; the functions F_1, F_2 etc. are subjected to the condition that their average value, taken over all systems of the ensemble must be a prescribed quantity. We might form different distributions, all satisfying the conditions. Now we seek the average value of η for all these different distributions; this average value of η will be a minimum for that ensemble where η is a linear function of F_1, F_2 etc. This is proved by GIBBS in his chapter XI. I shall call such a distribution a quasi-canonical distribution. The canonical distribution is nothing else but such a quasi-canonical distribution where there is only one function F_1 and that represents the energy. As the canonical distribution is of little application, e.g. not for systems of molecules with finite diameter, it would perhaps have been preferable to give a broader meaning to the word canonical and to use it in the sense, in which I use quasi-canonical. As GIBBS has however used the word canonical exclusively for ensembles for which $\eta = \frac{\psi - \epsilon}{\theta}$, I will use

the expression quasi-canonical for ensembles for which

$$\eta = \psi - aF_1 - bF_2 - \text{etc.}$$

In the ether we cannot have canonical ensembles, and so we will discuss only quasi-canonical ensembles. We put:

$$\eta = \frac{\psi - \epsilon}{\theta} - \frac{\varphi + \chi}{k} - \frac{\Omega_1 + \Omega_2}{\sigma_1} - \frac{\omega}{\sigma_2} \quad \dots \quad (8)$$

where, $d\tau$ representing an element of space:

$$\varphi = \int \left\{ \left(\frac{\partial g}{\partial z} - \frac{\partial h}{\partial y} \right)^2 + \left(\frac{\partial h}{\partial x} - \frac{\partial f}{\partial z} \right)^2 + \left(\frac{\partial f}{\partial y} - \frac{\partial g}{\partial x} \right)^2 \right\} d\tau \quad \dots \quad (9)$$

$$\chi = \frac{1}{16\pi^2 V^2} \int \left\{ \left(\frac{\partial \beta}{\partial z} - \frac{\partial \gamma}{\partial y} \right)^2 + \left(\frac{\partial \gamma}{\partial x} - \frac{\partial \alpha}{\partial z} \right)^2 + \left(\frac{\partial \alpha}{\partial y} - \frac{\partial \beta}{\partial x} \right)^2 \right\} d\tau \quad (10)$$

$$\Omega_e = \int \left(\frac{\partial f}{\partial x} + \frac{\partial g}{\partial y} + \frac{\partial h}{\partial z} \right)^2 d\tau \quad \dots \quad (11a)$$

$$\Omega_m = \int \left(\frac{\partial \alpha}{\partial x} + \frac{\partial \beta}{\partial y} + \frac{\partial \gamma}{\partial z} \right)^2 d\tau \quad \dots \quad (11b)$$

$$\omega = \frac{1}{\lambda} \int (f^2 + g^2 + h^2) \lambda d\sigma \quad \dots \quad (12)$$

k, σ_1 and σ_2 are constants, and σ_1 and σ_2 are infinitely small. The term $-\frac{\Omega_1 + \Omega_2}{\sigma_1}$ has been added, that we should have only to

deal with systems, consisting of free ether. Systems, containing electric masses are not absolutely excluded, but still their number is very small and may be neglected compared with that of the systems which are devoid of these masses. As $\frac{\partial \alpha}{\partial x} + \frac{\partial \beta}{\partial x} + \frac{\partial \lambda}{\partial y}$ is always zero, systems for which this expression has another value can never occur; yet we may admit them in such a small number, that they have no influence on the results. Finally we cannot take into consideration systems consisting of infinite space, for a finite quantity of energy would spread in it and we could not have a stationary distribution in the ensemble. Therefore it is necessary to enclose the electromagnetic energy within absolutely reflecting walls. But then it is necessary to add a term to η , which expresses, that the walls reflect absolutely, i. e. the quantities $[f]$ are always zero at the walls. The term $-\frac{\omega}{\sigma_2}$ expresses this; λ represents a small line in a direction normal to the surface; we make this line decrease indefinitely; $d\sigma$ represents an element of area.

If this distribution is to be for ether systems, what the canonical distribution is for material systems, then in the first place η must be a constant in time. For the other terms this is immediately evident, so we have only to show it for the term $\frac{\varphi + \chi}{k}$.

The relation, we have to prove may be written :

$$\frac{d\varphi}{dt} + \frac{d\chi}{dt} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

We will make use of the relations

$$\frac{d\alpha}{dt} = 4\pi V^2 \left(\frac{\partial \eta}{\partial z} - \frac{\partial h}{\partial y} \right) \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

$$\frac{df}{dt} = -\frac{1}{4\pi} \left(\frac{\partial \beta}{\partial z} - \frac{\partial \gamma}{\partial y} \right) \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

and of the following relations, that may be deduced from them :

$$\frac{d^2 f}{dt^2} = V^2 \left(\frac{\partial^2 f}{\partial x^2} + \frac{\partial^2 f}{\partial y^2} + \frac{\partial^2 f}{\partial z^2} \right) \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

$$\frac{d^2 \alpha}{dt^2} = V^2 \left(\frac{\partial^2 \alpha}{\partial x^2} + \frac{\partial^2 \alpha}{\partial y^2} + \frac{\partial^2 \alpha}{\partial z^2} \right) \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

and also of the corresponding relations for the other components. Now we have :

$$\frac{d\varphi}{dt} = \int \left[\left(\frac{\partial \eta}{\partial z} - \frac{\partial h}{\partial y} \right) \frac{d}{dt} \left(\frac{\partial \eta}{\partial z} - \frac{\partial h}{\partial y} \right) \right] d\tau \quad . \quad . \quad . \quad . \quad (18)$$

Integrating partially we get :

$$\frac{d\varphi}{dt} = \text{a number of surface integrals} -$$

$$- \int \left\{ \frac{df}{dt} \left(\frac{\partial^2 f}{\partial z^2} + \frac{\partial^2 f}{\partial y^2} - \frac{\partial^2 h}{\partial x \partial z} - \frac{\partial^2 g}{\partial x \partial y} \right) + \frac{dg}{dt} \left(\frac{\partial^2 g}{\partial z^2} + \frac{\partial^2 g}{\partial x^2} - \frac{\partial^2 f}{\partial x \partial y} - \frac{\partial^2 h}{\partial y \partial z} \right) \right. \\ \left. + \frac{dh}{dt} \left(\frac{\partial^2 h}{\partial y^2} + \frac{\partial^2 h}{\partial x^2} - \frac{\partial^2 f}{\partial x \partial z} - \frac{\partial^2 g}{\partial y \partial z} \right) \right\} dt. \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

In the coefficient of $\frac{df}{dt}$ in the cubic-integral we have :

$$- \frac{\partial^2 h}{\partial x \partial z} - \frac{\partial^2 g}{\partial x \partial y} = - \frac{\partial}{\partial x} \left(\frac{\partial g}{\partial y} + \frac{\partial h}{\partial z} \right) = \frac{\partial^2 f}{\partial x^2} \quad . \quad . \quad . \quad (20)$$

at least if we put, $\frac{\partial f}{\partial x} + \frac{\partial g}{\partial y} + \frac{\partial h}{\partial z} = 0$, so if we neglect the systems in

which electric masses occur. So we get for the coefficient of $\frac{df}{dt}$ the expression $\frac{1}{V^2} \frac{\partial^2 f}{\partial t^2}$ and for the cubic integral :

$$- \frac{1}{V^2} \int \left[\frac{df}{dt} \frac{d^2 f}{dt^2} \right] d\tau = - \frac{1}{16\pi^2 V^2} \int \left[\left(\frac{\partial \beta}{\partial z} - \frac{\partial \gamma}{\partial y} \right) \frac{d}{dt} \left(\frac{\partial \beta}{\partial z} - \frac{\partial \gamma}{\partial y} \right) \right] d\tau = - \frac{d\chi}{dt}.$$

As at the absolutely reflecting walls $[f]$ and therefore also $\left[\frac{df}{dt} \right]$ continue to be zero, the surface integrals disappear; so equation (13) is proved.

The quantities φ and χ which are introduced in order that the variation of the electric displacement and the magnetic induction may take place fluently, are defined as the sum of the squares of the components of the rotations of those vectors, if we disregard the coefficient $\frac{1}{16\pi^2 V^2}$ introduced in order that equation (13) may be satisfied.

This seems to me the simplest definition for φ and χ . It might, however, appear that we are not yet sure that $\frac{\partial f}{\partial x}$, $\frac{\partial g}{\partial y}$ and $\frac{\partial h}{\partial z}$ get convenient values. In order to show that this is not the case, we will prove the following relations

$$\varphi = \int \left[\left(\frac{\partial f}{\partial x} \right)^2 + \left(\frac{\partial f}{\partial y} \right)^2 + \left(\frac{\partial f}{\partial z} \right)^2 \right] d\tau \quad . \quad . \quad (21)$$

$$\chi = \frac{1}{16\pi^2 V^2} \int \left[\left(\frac{\partial \alpha}{\partial x} \right)^2 + \left(\frac{\partial \alpha}{\partial y} \right)^2 + \left(\frac{\partial \alpha}{\partial z} \right)^2 \right] d\tau \quad . \quad . \quad (22)$$

where again the brackets indicate that we have to take also the cor-

Botany. — "*On the prussic acid in the opening buds of Prunus.*"

By Prof. E. VERSCHAFFELT. (Communicated by Prof. HUGO DE VRIES).

During last winter and the spring of 1902 I made a series of determinations to ascertain the amount of hydrocyanic acid which can be prepared from different organs in species of *Prunus*. They were undertaken with the view of investigating the changes that occur during the budding, regarding the prussic acid-compounds. In these analyses the titration-method of LIEBIG was always used in the following manner. The parts of the plants to be examined — mostly 5–15 grs. freshly gathered material, — were heated in 200–300 cm.³ of water to 60° C., so as to kill the protoplasm without destroying the emulsin. Though it will directly be shown that this treatment answers the purpose, the heating to 60° was repeated after some hours or the next day, to be certain that no cells were still living. Between both treatments and also during 24 hours after the second heating, the organs remained, immersed in water, in a well corked flask, that the emulsin might have time to split completely the HCN-glucosides. After that, the distillation was performed, the prussic acid being collected in a little flask containing some drops of KOH-solution, and the titration was made after the method described in the treatises, with $\frac{1}{10}$ normal nitrate of silver. The distillate was always collected in a flask of 100 cm.³ capacity; by taking with a pipette a known volume, I was able to repeat the titration two or three times in the same experiment. The quantities of plant-material and water being as above, it appeared without exception that the whole of the prussic acid had been condensed together with the first 100 cm.³ of water.

The necessity of allowing the objects to macerate for some time after the killing is clearly shown by the following preliminary experiment.

From 25 leaves, one year old, of *Prunus Laurocerasus* (Bot. G. Amsterdam) gathered 9. 12. 01. the halves of the blades were cut on each side of the middle-nerve. The halves *a* weighed 11,85 grs., the halves *b* 11,35 grs. The first portion was immediately submitted to distillation after having been immersed in the proper quantity of water, and gave 0,0160 grs. HCN. The portion *b* was heated to 60° C., and remained under water till the next day; this time the amount of HCN was 0,0254 gr. As soon however as both portions are treated as *b*, the concordance of the results is very satisfactory:

12. 12. 01. 25 l., a.: 0,0223 gr., b.: 0,0226 gr. HCN.
 13. 12. 01. 25 l., a.: 0,0378 gr., b.: 0,0387 gr. HCN.
 10. 1. 02. 25 l., a.: 0,0239 gr., b.: 0,0242 gr. HCN.

In the same manner it could be ascertained that it was quite sufficient, after killing at 60°, to macerate during one day only, to obtain a complete splitting of the glucoside; also that the heating in 200—300 cm.³ at 60°, at two different times or even once, had left no living portions in the plant-organs.

The species studied were *Prunus Laurocerasus* L. and *Prunus Padus* L. It was chiefly my intention to follow the changes undergone by the prussic acid-compounds during the opening of the leaf-buds. As of both above named species the second is the earliest, and also yielded shoots a long time before the cherry-laurel, when cut branches were placed in the hot house, it was with *P. Padus* that the most complete experiments were made, those with *P. Laurocerasus* rather serving to control the former.

In the very first place, I asked myself the question whether the amount of HCN in resting buds — whatever might be the form of combination — did exhibit changes, when the buds began to grow. To know this, the estimation of the percentage in buds and young shoots issued therefrom is insufficient; one must compare the absolute quantity of prussic acid contained in a given number of buds with the amount in a same number of shoots. As the dimensions of both the buds and the shoots vary considerably, a satisfactory medium-value could only be obtained by the analysis of a great number of these objects, a precaution already made necessary on account of the buds being small.

The amount of HCN contained in resting buds of *P. Padus* will appear with sufficient exactness by the following three estimations:

10. 2. 02. 195 buds (Bot. G. Amsterdam); weight: 4,80 gr.-HCN: 0,0067 gr., i. e. 0,14 ‰; in 100 buds: 0,0034 gr.

11. 2. 02. 280 buds (B. G. Amsterdam); weight: 6,35 gr.-HCN: 0,0094 gr., i. e. 0,15 ‰; in 100 buds: 0,0034 gr.

20. 3. 02. 100 buds (B. G. Amsterdam); the buds are about to open, many show a green top); weight: 2,75 gr.-HCN: 0,0040 gr., i. e. 0,15 ‰; in 100 buds: 0,0040 gr.

In the first two analyses, the buds, as always was the case with the parts examined, in order to avoid losses of hydrocyanic acid, were immersed in water without being cut into fragments, and killed by heat. However, as it might be feared that the bud-scales should hinder the diffusion of glucoside and enzyme, the buds were, in the

third experiment, cut in halves, to see whether they should yield more HCN. As no marked difference was to be noticed, there surely was no prussic acid that in the first two instances had remained unestimated.

It was presently the turn of the opening buds to be studied. On the 2th of February cut branches of *P. Padus*, dipping in water, were placed on a well lighted spot in the hot house, the temperature being circa 20° C. After some weeks, a great number of buds had opened, and yielded shoots, which, though short, were nevertheless well furnished with leaves.

5. 3. 02. 75 shoots taken; weight: 5,20 gr.-HCN: 0.0079 gr., i. e. 0,15 ‰; in 100 shoots: 0,0105 gr.

Cut branches placed in hot house 26. 2. 02.

14. 3. 02. 60 shoots; weight: 8,70 gr.-HCN: 0,0108 gr.; i. e. 0,12 ‰; in 100 shoots: 0,0180 gr.

When one considers the weight of the shoots examined, it will be seen that in the second experiment they were more fully developed than in the first. It is clear that, as the shoots go on growing, a steadily increasing absolute amount of HCN-compounds gathers therein, so much so that even at a very early stage they contain three to four times the quantity found in the resting buds. As, on the other hand, the percentage of prussic acid depends on a number of circumstances, chiefly on the proportion of water in the shoots, a factor which itself is so very liable to modification, the changes undergone by this relative amount of HCN are much less interesting. It will however be noticed that, notwithstanding the fact that the weight of the young shoots exceeds many times that of the buds, the percentage of prussic acid is but feebly or not diminished.

I should wish to recall here that *Edm.* and *Em. Tuma*¹⁾, estimating the HCN in young leaf-buds of *P. Padus*, while these were opening in April, found no higher proportion than 0,05 ‰. This undoubtedly is due to the fact that the authors, distilling off after having added some sulfuric acid, did not obtain a complete splitting up of the glucosides.

It will now be asked, whether the prussic acid which appears in the growing shoots is formed in the same, or perhaps transferred to them from the branches. As the green unfolding leaves will very probably begin to assimilate, it seems credible enough that the hydrocyanic acid should be made by a process of "photosynthesis". Whether

1) *Zeitschr. Allgem. Oesterr. Apoth. Ver.* 1892, p. 330.

this is the case or not will easily be ascertained by analysing shoots developed in the dark.

Branches of *P. Padus*, placed in the hot house 10. 2. 02., covered by a blackened box. After some weeks, numerous etiolated shoots had been developed.

5. 3. 02. 50 short shoots taken; weight: 5,40 gr.-HCN: 0,0061 gr., i. e. 0,11 ‰; in 100 shoots: 0,0122 gr.

Branches put in the dark 24. 2. 02.

17. 3. 02. 30 well grown, etiolated shoots, for the most part $\frac{1}{2}$ — 1 dM. in length; weight: 7,90 gr.-HCN: 0,0054 gr.; i. e. 0,07 ‰; in 100 shoots: 0,0180 gr.

There can be no doubt, from the results given above, that shoots grown in the dark also contain a much larger quantity of HCN-compounds than the resting buds, and that these substances cannot have been built up by an assimilatory process, under the action of sunlight.

Results of quite the same kind were obtained in studying *Prunus Laurocerasus*.

Resting buds.-28. 12. 01. 115 buds, mostly axillar (from the growers of medicinal plants GROENEVELD and LINDHOUT, at Noordwijk); weight: 1,65 gr.-HCN: 0,0040 gr.; i. e. 0,24 ‰; in 100 buds: 0,0035 gr.

Shoots developed in the light (also mostly from axillar buds).-24. 4. 02. 50 shoots, still short, cut from the shrubs growing in the Botan. G. Amsterdam; the pale green leaves are not quite unfolded; weight: 9,30 gr.-HCN: 0,0278 gr., i. e. 0,30 ‰; in 100 shoots: 0,0556 gr.

27. 4. 02. 50 shoots, younger than the former, or newly opened buds; weight: 4,90 gr.-HCN: 0,0138 gr.; i. e. 0,28 ‰; in 100 shoots: 0,0276 gr.¹⁾

Etiolated shoots. — Branches of *P. Laurocerasus* (B. G. Amsterdam) placed in the hot house, under blackened cylinders 23. 4. 02.

10. 5. 02. 5 shoots taken; weight: 2,25 gr.-HCN: 0,0047 gr.; i. e. 0,21 ‰; in 100 shoots: 0,0940 gr.

Branches in the dark 25. 4. 02. 4. 5. 02. 10 very short shoots; weight: 1,65 gr.-HCN: 0,0037 gr., i. e. 0,22 ‰; in 100 shoots 0,0370 gr.

Branches in the dark 27. 4. 02. 12. 5. 02. 11 shoots; weight: 4,70 gr.-HCN: 0,0083 gr.; i. e. 0,18 ‰; in 100 shoots: 0,0755 gr.²⁾

¹⁾ A. J. VAN DE VEN. (*Cyaanwaterstofzuur bij de Prunaceae*. Dissertation Amsterdam. 1898; also Archives Néerlandaises, 2e Série, tome II, 1899 (reports (p. 34 resp. p. 391) for young shoots 0,19-0,23 ‰).

²⁾ VAN DE VEN (l. c. p. 37 resp. p. 393) applying the test of GRESHOFF—TREUB, was not able to detect prussic acid in etiolated shoots of *P. Laurocerasus*. This affords a new proof that microchemical reactions, as soon as the substances are not very abundant, necessarily require analytical confirmation. Mostly so when the test yields negative results.

Referring to what has been said with relation to *P. Padus*, the above given results require no further discussion. That in both species the percentage of HCN appears to be smaller in the etiolated shoots than in the green ones, has no very great importance. Etiolated shoots indeed are known to contain much more water, the evaporation being less active under the opaque bell-jar.

After it has thus been shown that buds opening in the dark also increase, as they grow, their amount of HCN, there still remain two ways of accounting for this augmentation. Perhaps the prussic acid — in whatever form it may be present — is made in the growing shoots out of other substances; it could however be drawn from other parts of the plants; that is to say the branches in *P. Padus*, possibly also the leaves in the evergreen *P. Laurocerasus*. I regret not to have succeeded in establishing with certainty which of the two explanations is the right one. All I can say for the present is that the HCN gathering in the shoots is not derived from the internodes, which bear the buds examined. However, the possibility of the acid being supplied by more distant parts cannot at the present time be said to be excluded completely.

In this part of the research, I again chiefly made use of *P. Padus*, as this species, bearing no leaves in winter, was especially favourable. The point to be ascertained was whether the increase of HCN in the opening buds should be accompanied by changes in the adjacent internodes.

In the first place the amount of HCN was determined in the internodes below resting buds. As the length and thickness of these organs are exceedingly variable, it once more was necessary to analyse a not too small portion of plant-material.

10. 2. 02. 100 internodes (Bot. G. Amsterdam); weight : 11,75 gr.-HCN : 0,0108 gr., i. e. 0,09%; in 100 internodes : 0,0108 gr.

7. 3. 02. 250 internodes (B. G.); weight : 18,95.-HCN : 0,0246 gr.; i. e. 0,13%; in 100 internodes : 0,0098 gr.

With these amounts will be compared those observed in the internodes below etiolated shoots.

Branches (B. G. Amsterdam) placed in hot house 24. 2. 02., and covered by opaque bell-jars.

17. 3. 02. 30 internodes are taken from below long etiolated shoots; weight : 3,85 gr.-HCN 0,0057 gr.; i. e. 0,15%; in 100 internodes : 0,0190 gr.

Already this first experiment does not prove in favour of the view, that the HCN-compounds should be drawn from the adjacent inter-

nodes. That this really is not the case will clearly be shown by the further analyses, in which were examined, on the one hand resting buds, on the other etiolated shoots, both with the corresponding internodes.

Resting buds — 18. 2. 02. 80 buds *P. Padus* (Bot. G.), and internodes bearing them; weight: 8,80 gr.-HCN: 0,0121 gr.; i. e. 0,14%; in 100: 0,0151 gr.

18. 2. 02. 125 buds and internodes; weight: 9,90 gr.-HCN: 0,0159 gr.; i. e. 0,16%; in 100: 0,0127 gr.

21. 3. 02. 100 buds and internodes (the buds beginning to open at the top for the greater part); weight: 8,35 gr.-HCN: 0,0092 gr.; i. e. 0,11%; in 100: 0,0092 gr.

29. 3. 02. 127 buds and internodes (cut on other shrubs as the foregoing; buds about to open); weight: 13,30 gr.-HCN: 0,0125 gr.; i. e. 0,09%; in 100: 0,0098 gr.

Young shoots. — Branches placed in the dark 24. 2. 02.

17. 3. 02. 30 shoots and internodes; weight: 11,75 gr. HCN: 0,0111 gr., i. e. 0,09%; in 100: 0,0370 gr.

Branches in the dark 24. 2. 02.; 25. 3. 02. 25 shoots and internodes; weight: 5,05 gr.-HCN: 0,0051 gr.; i. e. 0,10%; in 100: 0,0204 gr.

The considerable increase in the quantity of prussic acid: two to three times the original amount, shows clearly that it has not been augmented in the shoots at the cost of the internodes immediately belonging to the buds. I can even go farther, and suggest that neither it can have been supplied by the more distant internodes, one year old. In the analyses of shoots with the adjacent internodes, as well as in the experiment with internodes only, the material was taken from twigs developed the summer before, which in the experiment had yielded shoots at different heights. Therefore, if the more basal internodes had furnished the HCN-material for the shoots nearer the top, then the estimations would have shown it, since in that case so great an increase as was noticed would have been impossible. If consequently during the growth of the young shoots prussic acid might be drawn from the branches, it could be only from the older parts.

I should have liked very much to establish with certainty whether the shoots form themselves the hydrocyanic acid they contain. For that purpose I several times analysed branches of *P. Padus* as well as of *P. Laurocerasus*, so as to determine the amount of HCN present in the *entire* branches, before and after the opening of the buds. These estimations however did not yield satisfactory results, because, when the branches used were small, the buds in the dark only gave

short shoots, containing too small a quantity of HCN, and the difference between the two portions compared lay within the range of individual variation. If on the other side one will use larger branches, it is exceedingly difficult to choose two portions which can be compared; the limits of error of the experiment presently widen, and consequently the desired end is not reached. The experiments on branches longitudinally cut in two, which were undertaken with *P. Laurocerasus*, one moiety being immediately analysed, the other one, bearing the buds, being put in the dark till it had given off etiolated shoots, failed for the same reason. In consequence this question must remain unanswered for the present; perhaps experiments to be made next spring with rooted cuttings will meet with more success.

I will now endeavour to show that the cherry-laurel behaves in so far quite like *P. Padus*, that the parts situated immediately below the growing shoots retain their percentage of HCN nearly completely unchanged. Here the experiment becomes in a certain degree complicated, but also on the other hand is made more interesting, by the presence of the leaves. Therefore I must begin to tell something respecting the amount of HCN in these organs.

They have been analysed several times for pharmaceutical purposes. I only will recall here that FLÜCKIGER¹⁾ gave as the average of estimations, protacted during ten years, on cherry-laurels growing on the banks of the lake of Thune, 0,12% of the weight of fresh leaves. Folia Laurocerasi, bought in December and January from GROENEVELD and LINDHOUT, yielded 0,14—0,16%, while the shrubs grown in the Botanical Garden at Amsterdam were found to contain in their leaves an amount ranging from 0,12 till 0,21%, according to the individual analysed. Those were at least the quantities found in the course of the season December—May. The last named high figure is regularly yielded by the leaves of a certain shrub, that consequently could if wished be made the starting point of a selection to obtain a race containing much prussic acid.

It also may be of importance to acquire an idea of the absolute quantity of hydrocyanic acid contained in one leaf. Of course, owing to the variable dimensions of these organs, this quantity also varies considerably. I found 0,0015 — 0,0036 gr. HCN, the maximum-value in large leaves supplied by GROENEVELD and LINDHOUT, with a percentage of 0,15%.

Before studying the modifications in the amount of HCN in the

1) Pharmakognosie des Pflanzenreichs, 3e Aufl. 1891 p. 766.

leaves, brought about by the opening of the buds, also in the dark, one should know the changes caused by the occlusion of the light, independently of the formation of shoots. I properly ought to have done the same with the twigs of *P. Padus*, but nobody will, I trust, expect that these organs, with their peridermal coating, should show energetical processes of assimilatory kind.

The experiments with *P. Laurocerasus* took place not only with cut leaves, but also with branches bearing leaves. To examine whether cut leaves should change in the dark their amount of HCN, the halves of the freshly plucked organs were cut off along the middle-nerve and killed immediately. The other halves, with the middle-nerves still adhering to them, were brought in the hot house, and placed, under blackened bell-jars, in a glass, the petioli dipping in water. At the end of the experiment, the middle nerves were cut off, and the remaining halves of the blades analysed.

It appears that by staying even a fairly large number of days in the dark, the leaves undergo no modification whatever as regards the amount of HCN, at least not in winter ¹⁾.

25 leaves (Noordwyk). 13. 12. 01.

Halves *a* analysed immediately: HCN: 0,0135.

Halves *b*, after staying in the dark till 29. 12. 01., HCN: 0,0142 gr.

25 leaves (Noordwyk).

Halves *a*: 13. 12. 01., 0,0357 gr. HCN.

Halves *b*: 9. 1. 02., 0,0351 gr. HCN.

It follows that even after about one month no change whatever is to be noticed. Recently F. F. BLACKMAN and G. L. C. MATTHAEI ²⁾ have shown that the leaves of the cherry-laurel remain fresh and living in the dark even after fifty days. On the other side, the results given above quite agree with those obtained by A. J. VAN DE VEN ³⁾, using microchemical methods.

However, after a longer stay in the dark, or even, in certain cases, at a temperature of 20° C., after a shorter stay, pathological changes become noticeable in the leaves. Yellow spots, originating along the middle-nerve and the more important side-nerves, cover by and by the surface of the leaf till it becomes uniformly yellow. However, these organs don't die at once; they remain fresh many days, but the analysis shows that they lose rapidly their hydrocyanic acid.

¹⁾ J. COLARD (Journal de Pharmacie de Liège, 2e année, 1895 p. 1) states that leaves of cherry-laurel, when the entire shrubs remained in the dark from May till August, yielded a percentage of HCN, somewhat inferior to the percentage in plants exposed to the light.

²⁾ *Annals of Botany*, XV. 1901, p. 553.

³⁾ Dissertation Amsterdam. 1898, p. 35. *Archives Néerlandaises*, l. c. p. 392.

25 leaves (Noordwyk).

Halves *a*: 23. 12. 01., 0,0165 gr. HCN.

Halves *b*: 7. 1. 02., (beginning to show yellow streaks along the nerves): 0,0142 gr. HCN.

20 leaves (Bot. G. Amsterdam).

a: 27. 4. 02. 0,0162 gr. HCN.

b: 9. 5. 02. (yellow patches) 0,0113 gr. HCN.

25 leaves (Noordwyk).

a: 27. 12. 01. 0,0283 gr. HCN.

b: 20. 1. 02. (yellow) 0,0089 gr. HCN.

25 leaves (Bot. G. Amsterdam),

a: 17. 12. 01. 0,0283 gr. HCN.

b: 20. 1. 02. (yellow) 0,0067 gr. HCN.

Just the same processes can be observed, when cut branches bearing leaves are placed under opaque cylinders. The leaves can remain fresh and green many weeks, and keep their amount of HCN unaltered. The halves *a* of the blades were analysed immediately; the halves *b* remained, adhering to the middle-nerve, on the branches till the end of the experiment.

25 leaves, from branches placed in the dark 5. 12. 01.

a: 5. 12. 01. 0,0270 gr. HCN.

b: 22. 12. 01. 0,0283 gr. HCN.

25 leaves, from the same branches (5. 12. 01 in the dark).

31. 12. 01.; halves cut off; the other ones remain on the branches.

a: 0,0243 gr. HCN.

b: 16. 1. 02.; remaining halves yellow; it appears that in this stage they fall off, or sit but loosely on the branches: 0,0196 gr. HCN.

Branches placed in the dark 17. 12. 01.;

1. 1. 02.; 10 yellow leaves, about to be dropped; weight: 17,65 gr.-HCN: 0,0094 gr.; i. e. 0,05 %.

From the same branches I took the same day 25 fresh green leaves, and cut off the halves; weight: 13,15 gr.-HCN: 0,0229 gr., i. e. 0,17 %.

Halves *b*; 14. 1. 02 for the greatest part yellow, and falling off — HCN: 0,0155 gr.

This experiment therefore is also of importance, because it shows how the diminution in the amount of HCN goes clearly together with the discoloration and dropping of the leaves, and does not directly depend upon the length of the stay in the dark. In fact, when I placed separated branches in the hot house, but exposed them to the light, there always were a certain number of leaves that became

yellow; and in those the amount of HCN could also be shown to have diminished considerably.

Branches in hot house 26. 12. 01. Leaves yellow and falling off 22. 1. 02.; weight: 20,10 gr.-HCN: 0,0089 gr.; i. e. 0,04%.

Moreover, the same is the case with certain leaves directly taken from the shrubs grown in the Botan. G.

27. 4. 02.; 15 yellowish leaves are picked; weight: 24,95 gr.-HCN: 0,0158 gr.; i. e. 0,06%; in one leave: 0,0011 gr.

The figures for fresh leaves, mentioned formerly, show that but a small part of the HCN normally present had been retained here.

As the hydrocyanic acid was also observed to disappear from the cut leaves, when they became yellow, it seems very probable that this substance — or its compounds — are not transferred from the leaves to the branches, but must have undergone a chemical transformation.

The budding however, at least in the first periods that I examined, has no influence whatever on the quantity of prussic acid in the leaves and twigs. For instance, 30. 4. 02 were gathered, on the cherry-laurels of the Bot. G. Amsterdam, 10 leaves, one year old, each being inserted below a well grown young shoot; weight: 11,60 gr.-HCN: 0,0251 gr.; i. e. 0,22%; in one leaf: 0,0025 gr. These figures are of quite the same order as were yielded in December by the same shrub. 30. 4. 02 also were cut, below opening buds, twigs one year old; I chose intentionally twigs which though they bore numerous, and fairly big shoots, had no more leaves, these being cut or having fallen off at an earlier period, before the budding; weight: 8,25 gr.-HCN: 0,0086 gr., i. e. 0,10 %. I have found however, in twigs one year old, taken from the different shrubs in the Bot. G., during winter, a percentage of HCN ranging from 0,06 till 0,11 %. It is clear that there was no diminution after the opening of the buds.

Neither was this the case after the budding in the dark. Branches having been placed in the hot house, under darkened boxes, 29. 4. 02, leaves were cut 4. 5. 02, below etiolated shoots. The percentage: 0,14%, was the same as leaves from the same shrub had yielded before.

Finally, it could be shown in *P. Padus* that, though the young branches issued from the winter buds are already considerably developed, and bear numerous leaves of fair size, the amount of HCN-compounds in the internodes below is still the same as before the budding.

This was observed 25. 4. 02, when 130 internodes of *P. Padus*, from the year before, were taken below long shoots, well furnished

with leaves; weight: 10,90 gr.-HCN: 0,0140 gr.; i. e. 0,13 %; in 100 internodes: 0,0108 gr.

Resuming, I am brought to the conclusion that in both species of *Prunus* examined (*P. Padus* and *P. Laurocerasus*), when the buds open, there appears in the shoots growing from them a steadily increasing absolute quantity of HCN-compounds, whereas the percentage changes little in the period examined. In this same period at least, and at any rate for a great part, these substances appear independently of the light. Neither is this prussic acid drawn from the internodes directly bearing the buds, and developed the year before. Whether it is supplied by more distant organs, or is formed in the growing twigs out of other substances, this remains to be shown.

It is also still a point of research in what form the prussic acid is contained in the growing parts. That it is necessary to macerate the killed organs before the total amount of hydrocyanic acid can be distilled off, speaks in favour of the presence of a compound that can be split up by an enzyme. Moreover, as the liquid distilled from etiolated as well as from green shoots of *P. Padus* and *Laurocerasus*, has an intense smell of benzaldehyde, it is very probable that these organs also contain glucosides of the amygdalin-type.

Physics. — “*Observations on the magnetic rotation of the plane of polarisation in the interior of an absorption band*”. By Prof. P. ZEEMAN.

1. The difficulties of a complete theory of emission are partly avoided in a treatment beginning with the absorption, and this may have been the reason why VOIGT¹⁾ has followed this procedure, though it must be granted that in his method an explanation of the mechanism of the phenomenon as in LORENTZ's theory cannot be given²⁾. In VOIGT's theory the separation of a spectral line by the action of a magnetic field is found as the separation of an absorption line.

Some particulars in this separation were anticipated by this theory³⁾ and confirmed by experiment⁴⁾.

¹⁾ VOIGT. Wied. Ann. **67**, p. 345, 1899.

²⁾ For a comparison of the advantages of the theories of LORENTZ and of VOIGT, see LORENTZ. Rapports, congrès, Paris T. III. p. 16, 33, 1900. en Phys. Zeitschr. **1** p. 39, 1899. cf. also PLANCK. Sitz.ber. Ak. Berlin, p. 470, 1902.

³⁾ VOIGT. Drude's Ann. **1**, p. 376, 1900.

⁴⁾ ZEEMAN. Versl. Akad. Amsterdam. Dec. 1899. Archiv. Néerl. (2), **5**, p. 237.

The long since known phenomenon of the rotation of the plane of polarisation and the magnetic separation of the spectral lines were closely connected ¹⁾).

One result however of VOIGT's ²⁾ theory relating to the rotation of the plane of polarisation in the interior of an absorption band seemed to be in contradiction with the results of CORBINO ³⁾ or at least were not confirmed by the experiments of SCHMAUSS ⁴⁾ The theory of VOIGT requires a negative ⁵⁾ rotation of the plane of polarisation in the interior of an absorption band, CORBINO however only succeeded in observing a very small positive rotation.

It would be very remarkable however, if there existed a disagreement between theory and observation in this special field so closely connected with other well understood phenomena.

I have been experimenting already some time on this subject. In executing these experiments I have been aided in an excellent manner by Mr. HALLO.

I have succeeded in observing a negative rotation in the interior of an absorption band, the results of my observations being in perfect *qualitative* agreement with VOIGT's theory.

2. The method used in the following observations on the rotation in sodium vapour is principally the same as that which has been used by VOIGT ⁶⁾ in his demonstration of the double refraction of sodium vapour placed in a magnetic field. Already HUSSEL ⁷⁾ used it in a determination of the natural rotation of the plane of polarisation in quartz, and also CORBINO in his first experiments on sodium.

By means of a system of quartz prisms (as has been used by FRESNEL in his experiment on the division of a plane-polarised ray into two circularly polarised rays) a number of horizontal interference fringes are formed in a spectrum. The light traverses the prism in the direction of the axis and the edges are horizontal and perpendicular to the slit of the spectroscope. The prism system (length 50 mm.) was placed in my experiments as near as possible before the slit of spectral apparatus and a small Nicol, used as analysator, behind the slit. The polarising Nicol was placed, of course, before the electro-

¹⁾ cf. also LARMOR. Aether and Matter, p. 203.

²⁾ VOIGT. Ann. der Physik, (4), 6, p. 784, 1901.

³⁾ CORBINO. Atti R. Acc. dei Lincei. Vol. 10 p. 137, 1901, Nuovo cimento Febbraio 1902.

⁴⁾ SCHMAUSS. Ann. d. Phys. 2 p. 280, 1900.

⁵⁾ The magnetic rotation in the vicinity of the band is positive in sodium vapour.

⁶⁾ VOIGT. Wied. Ann. 67, p. 360, 1899.

⁷⁾ HUSSEL. Wied Ann. Bd. 43, p. 498, 1891.

magnet (of the RUHKORFF type). The spectroscope was a ROWLAND'S grating, for which I am indebted to the kindness of the Directors of the Dutch Society of Sciences at Harlem; it has a radius of 6.5 M., 10.000 lines to the inch and a divided surface of nearly 14 cm.

The grating was mounted for parallel light in the manner indicated by RUNGE and PASCHEN ¹⁾. The source of light was in most cases the electric arc, in some the sun.

Using this arrangement of the experiment we can deduce immediately from the deformation of the interference fringes in the neighbourhood of the absorption bands, when the sodium vapour is under the action of the magnetic field, the value of the rotation of the plane of polarisation for different wave lengths. Fig. 1 of the Plate gives an idea of the aspect of the fringes in absence of the field in the neighbourhood of the sodium lines, rather much sodium being present in the flame between the poles. The observations were made in the second order.

3. In the experiments first to be described, the distance between the perforated poles was about 4 m.m. and the intensity of the field about 15.000 c. g. s. units. In this field was placed a gas flame fed with oxygen and a small quantity of sodium introduced in it by means of a glass rod. After removal of the polarisator and of the FRESNEL prism the two doublets, in which the sodiumlines are separated, in the inverse magnetic spectral effect were observed. Between the components of the doublet were seen the very narrow reversed sodiumlines due to the arc light itself.

The polarisator and the prism were now introduced in their proper places. The field of view was then crossed by the above mentioned (2) dark, nearly horizontal interference fringes.

I now wished to ascertain the deformation of the fringes by increasing continuously the quantity of sodium vapour, the field remaining constant. This method must be preferred for obvious reasons to the other which might have been followed also, viz: the examination of a flame with constant percentage of sodium under varying magnetic intensities.

The following observations refer to D_1 :

If the quantity of sodium in the magnetic field was only extremely small, the interference fringe exhibited at the place of the reversed sodium line a protuberance — let us say *downward* — the lines of the doublet being somewhat stronger just above the interference fringe. In fig. 1 this behaviour is represented schematically.

¹⁾ KAYSER. Handbuch. Bd. I, p. 482.

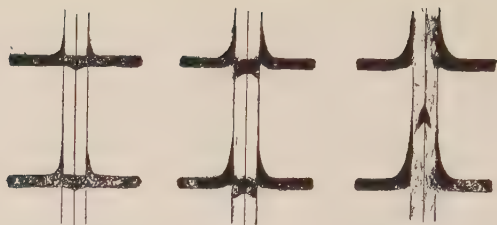


Fig. 1.

Fig. 2.

Fig. 3.

Increasing now the quantity of sodium (always remaining very small however, absolutely) the interference fringes moved upward along the components of the doublet, whereas the part of the fringe between the components seemed no longer connected to the exterior fringes and accepted the shape figured schematically in fig. 2.

Increasing still further the density of the vapour the interior part of the fringe slid downward with increasing velocity and then resembled an arrow with point directed upward, the parts more removed from the medium line fading away and disappearing (cf. the schematic fig. 3). At last the arrow entirely disappeared by the increase of the density of the vapour. It then became impossible to distinguish the fringes or any trace of structure in the field between the components. Rather much light was transmitted. The entire width of the components of the doublet was now about of the same order as the distance of their central lines.

A further increase of the quantity of sodium obscured the central part more and more (see further (8)).

The exterior fringes moved continuously upward while the density was being increased.

In a field of about 20000 units the downward displacement could be followed over a distance of more than the double of the distance between two fringes, corresponding to a *negative* rotation of above $2 \times 180^\circ$, say 400° . The distance between the poles was 4 mM.

Some more accurate data will be given on another occasion.

In the case of D_2 the phenomena were in the main of the same character.

For D_2 it was however characteristic that the stage of the nearly or entirely vanishing of the interior fringes was reached with smaller field, whereas also the shape of the interior fringe differed from the one observed in the case of D_1 . Hence there exists also in this case a difference between D_1 and D_2 , a difference already known to exist in the phenomena of reversal, of the separation by a magnetic field and of the rotation of the plane of polarisation in the vicinity of the absorption band.

4. It appeared possible to keep stationary each of the stages described in (3) during a considerable time. Excellent photographs could be secured with plates which were sensitised for yellow light with erythro-sine silver. Instead of the gasflame fed with oxygen it was easier, in the case of greater distances between the poles, to use a Bunsen burner wherein common salt was introduced.

5. If the density of the vapour was maintained as constant as possible and if it and the fieldintensity corresponded to the circumstances represented in fig. 3 (3) then an *increase* of the field gave a motion of the arrow (fig. 3) (3) upwards, corresponding to a *decrease* of the negative rotation and reciprocally. It was possible to observe by eye observation very clearly this decrease when the field was changed e. g. from 18000 to 25000. If the circumstances were more in accordance with fig. 2 (3) then the same change of field produced a change only just perceptible of the negative rotation but in the same sense as mentioned in the case of fig. 3.

An enlarged reproduction of one of the photographs is shown in fig. 2 of the plate. The distance between the poles in this experiment was 6,3 mM., the field intensity about 14000¹⁾. The negative rotation in the case of D_1 is somewhat less than 90° . In the case of D_2 yet only some traces of the interior fringes can be seen (3). The negative rotation is about 180° . In the photograph are seen also the reversed very narrow D_1 -line and the broader D_2 -line, which are due to the arc itself and have nothing to do with our subject.

6. The observations (3, 4, 5) agree qualitatively in an excellent manner with the conclusions from VOIGT's theory. According to it, the negative rotation must be of the same order of magnitude as the positive one. This last was known from MACALUSO's and CORBINO's experiments to be very great. The enormous value and the sign of the negative rotation given in (3) may thus be regarded as a beautiful confirmation of the theory.

As much is this the case with the direction (5) of the change of the negative rotation with increasing field. In order to see this we must know the value of the quantity occurring in the theory $P = \frac{cR}{\mathfrak{P}}$ (R = fieldintensity, c and \mathfrak{P} parameters of the absorptionband), for which the comparison must take place. It was possible to assign a value to P by comparison of the phenomenon with VOIGT's figure 1²⁾.

¹⁾ The intensities of the field were measured by means of a bismuth spiral in the centre of the field. Probably the values given are somewhat too high. Measurements of the magnetic change of the spectral lines give lower values.

²⁾ Annalen der Physik, 6 p. 789. 1901.

This figure gives $n\chi_0$ (χ_0 angle of rotation, n a mean value of the index of refraction) as function of a certain variable Δ , whereas our phenomenon is a representation of χ_0 as a function of λ . Reducing the abscis of the mentioned fig. 1 to $1/_{20}$ or $1/_{25}$ we obtain diagrams resembling in the main features fig. 2 of the Plate. To the greater observed negative rotation (3) correspond values of P , which can be estimated at 5 or 8. The smallest easily observed rotations in the used strong field are probably in the vicinity of the critical value $P=1.73$.

7. The slope of the exterior interference fringes is greater towards the side of the greater wavelengths than towards the violet, at least so far as the rotation due to one band does not influence visibly the rotation due to the other. At the same distances, if not very small, of each of the two D lines the rotation at the side of the violet is greatest. The interior fringes also show a slight asymmetry, so e. g. the point of the arrow in fig. 3 (3) ought to be asymmetrical. The part at the side of the violet is predominating.

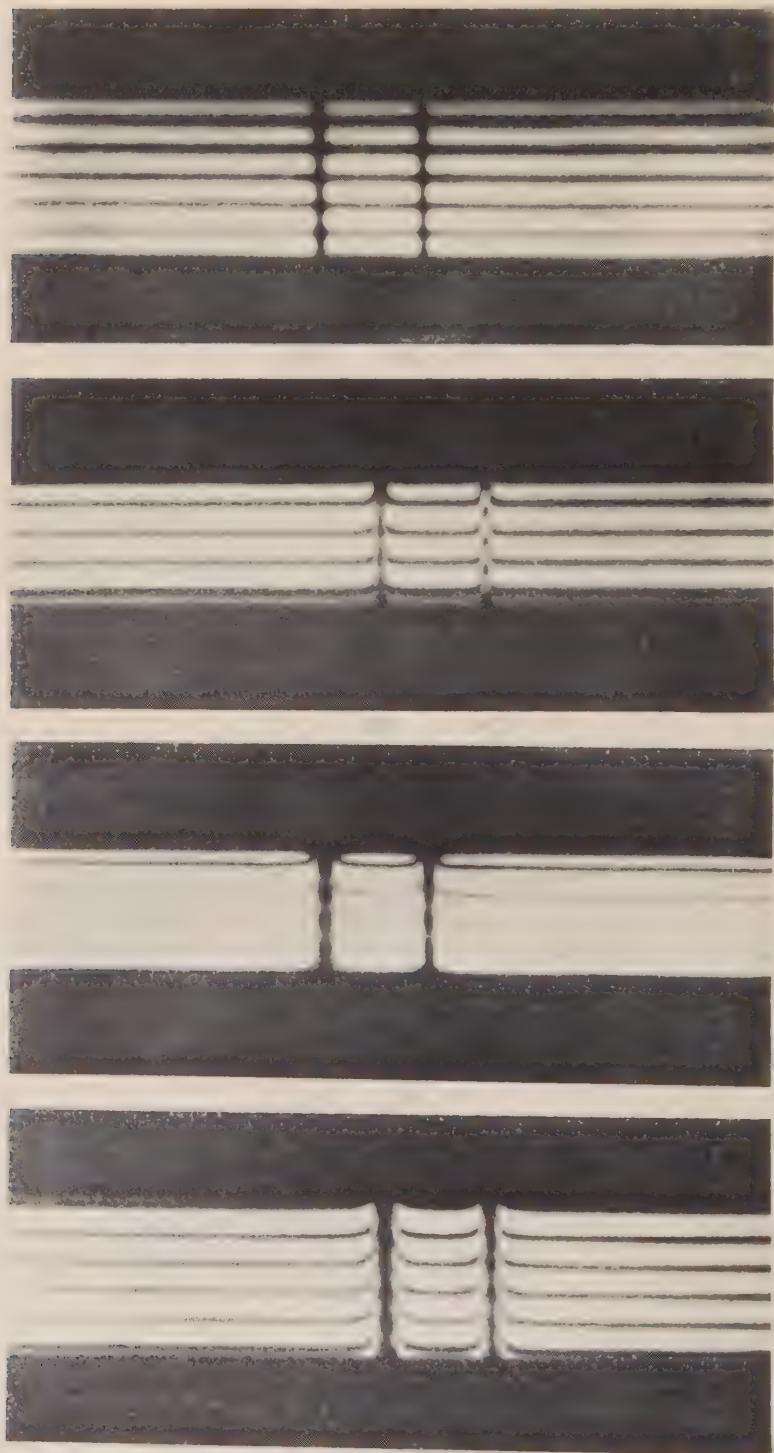
It is clear that these phenomena depend upon an asymmetry of the dispersion curve.

8. With very dense sodium vapour, hence under circumstances which are beyond the last stage of (3), I observed phenomena very probably identical with those observed by CORBINO. In my first experiments with those dense vapours I thought it absolutely necessary for securing sufficient intensity to widen the slit beyond the width used in the already given experiments. I now see however that this is unnecessary.

Using these very dense vapours one sees in the absorption band a horizontal part of an interference fringe, which seems to have undergone a very small displacement *upwards* by the action of the field. These horizontal parts are more ill-defined and broader and the whole phenomenon in the bands is darker than under the circumstances described in (3), (4), (5).

Figs. 3 and 4 of the Plate will give a clearer impression of the change in the phenomenon than a long description.

Fig. 3 was obtained with a field of 4500 units and much sodium. I have made some measurements, according to a method not to be given here, concerning the displacement of the central (in horizontal and vertical direction) part of the interference fringe, and I have found a displacement, which would correspond to a *positive* rotation of about 8° with both D -lines. Fig. 4 was taken with a field of 10700 and much sodium. The exterior interference fringes are very clear and much deformed; the rotation in the parts adjacent to the absorp-



tion band surpass 180° . The interior interference fringes are very indistinct. Their appearance would suggest that in the case of D_1 in Fig. 4 the stage has been scarcely surpassed, reached for D_2 in fig. 2.

This however cannot be the case because there was too much sodium in the flame. A comparison with fig. 2 will show that the lines are much broader in fig. 4. Measurements taken on other negatives gave me for fields of 11000, displacements of about $\frac{1}{16}$ of the distance between two fringes, corresponding to a positive rotation of 11° . Hence the displacements in these cases are precisely of the same order of magnitude as in CORBINO's experiments. The paleness of the borders of the band is easily accounted for by the remark that there the intensity one of the circularly polarised rays largely exceeds the other.

I do not believe that these facts are in contradiction with theory. It is true that it requires for very high values of P a value zero for $(n\chi_0)_T$. If we must take as the locus of the fringe the mean vertical height, then really the rotation would be positive. It seems possible that with those broad fringes the case is different. It is also possible that the circumstances, assumed in the theory are not wholly realised in the experiments with dense vapours. I am making some new experiments about this subject and therefore shall not discuss further the different possibilities.

EXPLANATION OF THE PLATE.

The Plate gives about sixfold enlargements of the photographs.

Fig. 1. Interference fringes and absorption lines in absence of the field and rather much sodium. (2)

Fig. 2. Same lines. Field intensity about 14000, little sodium. (3) (5)

Fig. 3. Same lines. Field intensity about 4500, much sodium. (8)

Fig. 4. Same lines. Field intensity about 10700, much sodium. (8)

Anatomy. — "*A new Method for demonstrating cartilaginous Mikroskeletons.*" By Prof. J. W. VAN WIJHE.

It is a well-known quality of cartilage that it firmly retains certain anilinstains. Taking advantage of this quality, I have for some years endeavoured to find a stain, which will remain permanent in the cartilage, after it will have been entirely extracted out of the other tissues. If the object is made transparent in canada balsam, the cartilaginous skeleton will then be seen as if it were prepared. I was more or less successful with most of the so-called basal anilin-pigments, best of all however with methylene-blue, and so I was induced to use this latter stain exclusively.

The coloring of the cartilage was attempted with full-grown objects as well as with embryos, but as the coloring-method is chiefly useful when applied to small objects, with which the ordinary preparation-method proves deficient, it will chiefly be applied to embryos.

Whenever we wanted to examine the cartilaginous skeleton of an embryo, we were, up to the present time, obliged to make series of sections and to construct an enlarged model after these sections, all of which took up a good deal of time. As a rule it would have taken much too long to model a whole skeleton; therefore in most cases only a part was constructed, for instance the head-skeleton or the pelvis.

Working on this plan a single object requires many months of labor, and besides at the end you have not the object itself, but an imitation.

Following the coloring-method, on the contrary, a great number of entire skeletons are obtained in a short time with little trouble, not clumsy imitations, but the objects themselves with all parts in their natural connection and the contours of the whole embryo and of different organs besides, for notwithstanding the transparency of the organs the outlines of many are still clearly recognizable. Although the cartilage is colored intensely blue, it remains transparent: so for instance the spinal column glimmers through the shoulder-blade.

The method is as follows:

The embryo is fixed in the usual way in 5% sublimate-solution, or 10% formol, or in ZENKER's liquid and is preserved in alcohol. No doubt it may be fixed in many other ways; I even obtained useful results with old preparations of alcohol from the collection. I mostly fix the embryos in 5% sublimate-solution, to which is added $\frac{1}{10}$ volumen formol, shortly before using.

The object may now be brought immediately from the alcohol into the pigment-solution, but it has seemed advisable to me to extract previously for a day or two with alcohol, which contains some ($\frac{1}{4}$ %) hydro-chloric acid. The acid alcohol must be renewed if it has turned yellow the next day, which often happens when iodine has been used in extracting the sublimate. The iodine is fatal for the coloring, as it forms with methylene-blue an almost insoluble precipitate and with neutral alcohol the iodine cannot be quite removed. This is proved when seemingly white objects, preserved for a year and more in alcohol which has remained colorless, being brought into acid alcohol, cause this liquid to turn yellow the next day. The yellow color disappears after the addition of a few drops of sublimate-solution.

From the acid alcohol the object is placed for a day at least, rather for a week, into an alcoholic solution of methylene-blue, to which 1% hydro-chloric acid has been added. It is sufficient when $\frac{1}{4}$ gram of methylene-blue is dissolved in 100 cc. alcohol of about 70 %. If more coloring-matter is taken, a sediment remains on the bottom of the bottle. After the addition of the hydro-chloric acid, blue crystalline needles separate themselves from the liquid. For this reason it is desirable that this addition should be made not at the moment of using, but some time before.

The object when taken from the pigment, should not show any sediment. If it does, it has not been extracted long enough with acid alcohol. Although it is not lost yet, it may cost months before the sediment is removed. The intensely blue-colored object is treated in the usual manner in the above mentioned acid alcohol, which is renewed several times on the first day and once daily afterwards. The renewal is continued until the alcohol shows no blue tinge the next day. The time required for this is, of course, dependent on the size of the embryo. This time can be shortened by taking alternately alcohol of about 70% and a stronger one and hanging the object one day in the stronger alcohol, whereas the next day it is allowed to settle on the bottom of the bottle; this is not necessary however. In about a week the stain has been removed from all the tissues, except from the fundamental substance of the cartilage. It is not necessary anxiously to observe the day when the alcohol shows no more coloring; objects kept for a year and longer in the colorless acid alcohol, showed the cartilage still distinctly blue.

The object is now dehydrated in absolute alcohol, in the usual way, and rendered transparent in xylol. To avoid wrinkles, it is not put immediately from the alcohol into xylol, but first in a mixture of two parts of absolute alcohol with one part of xylol, then in a mixture of one part of absolute alcohol with two parts of xylol and only after that in xylol only. Larger-sized embryos are cut in halves or in different pieces with the razor. After that the objects are put first in a thin, afterwards in a thick solution of canada-balsam in xylol and finally in a solution, which in ordinary temperature is solid, but liquid at 60°. In this solution they remain in the thermostat at 60° during a couple of hours and are then enclosed in glass-cells under a covering-glass.

The glass-cells in trade are usually too low, higher ones can easily be obtained by fixing stripes of window-pane with canada-balsam on an object-glass.

My experience has not been long enough to enable me to assure that the objects will not fade in the long run, I can only say, that even my oldest preparations, which have been enclosed in canada-balsam for a couple of years, have not faded visibly. I have taken care however to dissolve in xylol the solid, neutral canada-balsam of GRÜBLER's myself because the commercial solution often contains turpentine.

The staining method here described has been successful with the cartilaginous skeleton of representatives of all classes of vertebrate animals, as for instance with *Amphioxus*, with embryos of sharks and rays, of salmon and roaches, of frogs and lizards, of birds, of mice, rabbits and man.

With regard to man, it is of importance that the coloring can still be successful with embryos in a far proceeded state of dissociation and which otherwise one would be inclined to throw away.

Magnified slightly, the preparations are particularly suitable for demonstration. I here demonstrate the skeleton of a human embryo of about five weeks old and draw your attention to the rudiment of the shoulder-blade. It is still exclusively adjacent to the neck, on a level with the 5th, 6th and 7th cervical vertebrae, with the point still above the first rib. Eleven ribs show the blue color of the cartilage, the undermost, the twelfth, not yet.

In this second embryo, which is somewhat older, the shoulder-blade has left the 5th cervical vertebra and lies on a level with the 6th and 7th cervical- and the 1st and 2^d thoracic vertebrae; it reaches with its point as far as the third rib. Not only all the twelve ribs are visible on the twelve thoracic vertebrae, the rudiment of a rib on the last cervical vertebra is seen besides, which rudiment fuses with this vertebra later on, as is well-known.

In this third embryo, which I received in perfect condition and which after fixation was 25 mm. long in its natural curve, it may be seen that the shoulder-blade has again gone down a little. At the neck it does not reach higher than the level of the last cervical vertebra and reaches with the point as far as the 4th rib. Further the rudiment of the pelvis may here be noticed, on the level of the fourth lumbar — and the first sacrum-vertebrae and on the head the cartilage of the occiput, the ear case, the cartilage of MECKEL and the rudiment of the incus.

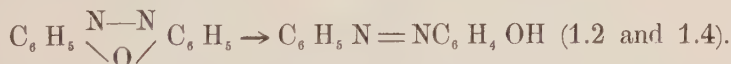
Other preparations show the paired rudiment of the rabbit's and the chicken's sternum.

Also for macroscopic museum-preparations this is a suitable method; I could show you, for instance, the cartilaginous skeleton of shark-

embryos more than 2 dm. long, preserved in xylol. These preparations were exceedingly beautiful at first and the non-cartilaginous tissues transparent, as clear as crystal; later on however they lost the transparency for the greater part and became opalescent. The cause of this change is unknown to me. Such macroscopic preparations ought therefore also to be enclosed in canada-balsam or dammar-resin.

Chemistry. — "*Intramolecular rearrangement of atoms in azoxybenzene and its derivatives.*" By Dr. H. M. KNIPSCHER. (Communicated by Prof. LOBRY DE BRUYN.)

WALLACH and BELL¹⁾ noticed a long time ago that azoxybenzene is converted into its isomer *p*-azoxybenzene by gently heating it with sulphuric acid, or by means of fuming sulphuric acid at the ordinary temperature. BAMBERGER found that in this process there is also formed half a percent of *o*-oxyazobenzene a substance discovered by him some time ago when acting on nitrosobenzene with aqueous caustic soda at 100°. The reaction noticed by WALLACH and BELL must be represented as follows :



Sulphuric acid was up to the present the only reagent capable of causing the said intramolecular rearrangement of atoms. WACKER²⁾, however, when stating in his paper on *α*-azoxynaphtalene that this substance turns red by exposure to direct sunlight, also remarks that azoxybenzene is likewise sensitive to sunlight, but he only mentions that it turns deep yellow without having investigated the nature of the change.

Various derivatives of azoxybenzene also appeared to be liable to the same intramolecular rearrangement of atoms, but again sulphuric acid is mentioned as the only reagent capable of causing the change. The result of those investigations showed that some of the substitution products, namely the meta-derivatives, are almost quantitatively converted into the isomeric phenols, while the ortho- and para-derivatives are only affected to a small extent or not at all.

¹⁾ Ber. **13**. 525 (1880).

²⁾ Ber. **33**. 3192 (1900).

³⁾ Ber. **33**. 1939 (1900).

⁴⁾ Ann. **317**. 313 (1901).

SCHULTZ scarcely obtained any dichloro-oxyazobenzene when treating *p-p*-dichloro-azoxybenzene with fuming sulphuric acid, but *p-p*-dichloro-azobenzene was formed; *m-m*-dichloro-azoxybenzene however yielded *m-m*-dichloro-oxyazobenzene in large quantity.

KLINGER and PITSCHKE⁵⁾ succeeded in almost entirely converting *m-m*-dinitro-azoxybenzene into *m-m*-dinitro-oxyazobenzene by heating the same with sulphuric acid at 140°. By heating *o-o*-azoxytoluene with sulphuric acid at 100°—120° they could only obtain *o-o*-azotoluene accompanied by acids such as *o*-tolylazobenzoic acid.

LIMPRICHT¹⁾ converted azoxytoluidine into oxyazotoluidine in an analogous manner, whilst ELBS and SCHWARZ²⁾ succeeded in converting *p-p*-diamino-*o-o*-azoxytoluene into *p-p*-diamino-*o-o*-oxyazotoluene by heating it with sulphuric acid at 100°—105°.

My object now was to ascertain whether the above described intramolecular rearrangement might be realised by other means than by the use of sulphuric acid. It was ascertained that the intramolecular rearrangement of atoms in azoxybenzene is also possible by raising the temperature to at least 200° and by the influence of direct sunlight. In the first case a mixture is formed of *p*- with much *o*-oxyazobenzene; in the second case only *o*-oxyazobenzene is obtained. None of these changes is reversible. Also those derivatives of azoxybenzene which undergo intramolecular rearrangement by the action of H₂SO₄ are converted by the said agencies, but the action is slower and the amount is smaller than that obtained from azoxybenzene. The investigation of these derivatives has not yet been quite concluded.

Acetic anhydride is without effect on azoxybenzene at the boiling temperature; on heating however at 200° the change already takes place in a notable degree, much better than by merely heating the substance itself, while an acetate is either not formed at all, or only in very small quantity. *P*-oxyazobenzene is not formed at 200° but only the *o*-isomer. Solutions of azoxybenzene derivatives in acetic anhydride do not however suffer any intramolecular change at 200°.

Addition of Zn Cl₂ or P₂O₅ to acetic anhydride does not enable it to cause the change at the boiling point; heating with the so-called BECKMANN's mixture is also without avail. By heating a solution of azoxybenzene in this mixture at 150° and 180° it appears that azoxybenzene which, when prepared in the ordinary way is a yellow substance, is perfectly white when in a pure condition. The ordinary

⁵⁾ Ber. **17**, 464 (1884).

⁶⁾ Ber. **18**, 2552 (1885).

¹⁾ Ber. **18**, 1405 (1885).

²⁾ Journ. f. pr. chem. **171**, 567 (1901).

product therefore contains a yellow impurity, which cannot be removed by recrystallisation.

The intramolecular change was attempted in vain by means of the following reagents :

Acetyl chloride, butyryl chloride, benzoyl chloride, phosphorus pentachloride, phosphorus oxychloride, phosphoric acid, aluminium chloride, aqueous caustic soda, copper oxide, zinc oxide and zinc carbonate. Of these reagents the following deserve to be specially mentioned on account of their action on azoxybenzene :

Acetyl chloride : formation of *p-p*-dichloro-azobenzene and *p*-chloro-acetanilide ; benzoyl chloride : formation of azobenzene ; phosphorus pentachloride : formation of azobenzene with evolution of chlorine ; aluminium chloride : formation of *p*-chloro-azobenzene.

Mathematics. — "*On the connection of the planes of position of the angles formed by two spaces S_n passing through a point and incident spacial systems.*" By Prof. P. H. SCHOUTE.

1. If in a space S_{2n} with $2n$ dimensions two spaces S_n are given arbitrarily, these have in general only a single point O in common and they form in this point with each other n angles differing in general respectively. These angles are situated in n definite planes through O and the line at infinite distance of such a *plane of position* has a point in common with the two given spaces $S_n^{(1)}$, $S_n^{(2)}$ as well as with the spaces $S_n'^{(1)}$, $S_n''^{(2)}$ drawn perpendicular to the just named spaces through any arbitrary point, say O , not at infinite distance. In this way the two planes of position of two planes ε_1 , ε_2 taken arbitrarily in S_4 are determined by the common transversals of four lines situated in a three-dimensional space, viz. of the lines g_1 , g_2 of ε_1 , ε_2 in the space S_3 at infinite distance in S_4 and the lines g_1' , g_2' , normally conjugate in this S_3 to g_1 , g_2 .

2. Let us consider the particular case when the n angles formed by $S_n^{(1)}$, $S_n^{(2)}$ are alike ; as an introduction we take in S_4 again two planes ε_1 , ε_2 forming with each other in their point of intersection O two equal angles. It is known that in that case the four above mentioned lines g_1 , g_2 , g_1' , g_2' are generators of an hyperboloid ; so they admit of not only two but of an infinite number of common transversals, to which answer likewise an infinite number of planes of position. If the system of those transversals t is indicated by (t) , the

system of the lines g intersecting all the lines (t) by (g) , there exists between the two incident systems of lines (g) , (t) at infinite distance this reciprocal connection that the plane passing through an arbitrarily chosen point O at finite distance and an arbitrary line of one of the two systems is a plane of position for the pair of the planes connecting the point O with two arbitrary lines of the other system. From the manner in which the quadratic scroll (t) is formed out of g_1, g_2, g_1', g_2' namely ensues that the surface H^2 of order two, bearer of the two systems (g) , (t) , agrees with itself in the polar system at infinity in S_4 of which the imaginary sphere B_∞^2 common to all hyperspheres is at the same time the locus of the points lying in their polar planes and the envelope of the planes passing through their poles; for to each line t intersecting g_1, g_2, g_1', g_2' regarded as locus of points agrees in that correspondence a line t' lying with g_1', g_2', g_1, g_2 in a plane regarded as axis of a pencil of planes, etc.

If we make the lines g, g' of (g) normally conjugate to each other to correspond to each other, then between the lines of (g) a quadratic involution is formed; the double rays g_i, g_j of this involution must lie on B_∞^2 , being normally conjugate to themselves. Likewise does B_∞^2 contain the double rays t_k, t_l of the involution formed in quite the same way between the lines t, t' normally conjugate to each other. So H_∞^2 and B_∞^2 intersect each other in the sides of a skew quadrilateral whose pairs of opposite sides are the double rays (g_i, g_j) and (t_k, t_l) of the pairs of rays (g, g') and (t, t') of (g) and (t) normally conjugate to each other.

If (g, g') are two normally conjugate rays g and (t, t') likewise two normally conjugate rays t and if we take the planes Og, Og' and Ot, Ot' as coordinate planes OX_1X_2, OX_3X_4 and OX_2X_3, OX_4X_1 , then the surface H_∞^2 must be characterised with respect to this rectangular system of coordinates by the equation $x_1x_3 = x_2x_4$ between the infinite coordinates. For the quadratic surface $x_1x_3 + \rho x_2x_4 = 0$, brought through the lines at infinite distance of the four mentioned coordinate planes, corresponds to itself in the polar system with the sphere $x_1^2 + x_2^2 + x_3^2 + x_4^2 = 0$ at infinite distance as surface of incidence only when the absolute value of ρ is equal to unity. For the normally conjugate line of $x_1 = \lambda x_3, \lambda x_2 + \rho x_4 = 0$ is $\lambda x_1 + x_3 = 0, \rho x_2 = \lambda x_4$ and this new line lies only for $\rho^2 = 1$ with the original one on $x_1x_3 + \rho x_2x_4 = 0$. So by reversing if need be the sign of one of the coordinates we can always bring the equation of H_∞^2 into the form $x_1x_3 = x_2x_4$.

3. Before passing on to the general case we shall consider the

case, when in S_3 two three-dimensional spaces $S_3^{(1)}, S_3^{(2)}$ are given arbitrarily. The line g_∞ at infinite distance of the plane of position of one of the angles formed by those spaces in their point of intersection O is then a common transversal of the planes at infinite distance $\varepsilon_\infty^{(1)}, \varepsilon_\infty^{(2)}$ of $S_3^{(1)}, S_3^{(2)}$ and the planes $\varepsilon_\infty'^{(1)}, \varepsilon_\infty'^{(2)}$ normally conjugate to these. As the common transversals g_∞ of the three planes $\varepsilon_\infty^{(1)}, \varepsilon_\infty^{(2)}, \varepsilon_\infty'^{(1)}$ form a "variety" V_3^3 of order three of three dimensions and this curved space is intersected in three points by $\varepsilon_\infty'^{(2)}$, the spaces $S_3^{(1)}, S_3^{(2)}$ make in O three angles with each other. This variety V_3^3 is not only (compare i. a. the first part of my "Mehrdimensionale Geometrie", vol. XXXV of the Sammlung SCHUBERT", N^o. 102, 103) the locus of a twofold infinite series of transversals g_∞ , but at the same time the locus of a simple infinite series of planes ε_∞ , each of which determines with $\varepsilon_\infty^{(1)}, \varepsilon_\infty^{(2)}, \varepsilon_\infty'^{(1)}$ on the lines g_∞ quadruples of points with a definite anharmonic ratio, i. e. V_3^3 is the bearer of two incident systems which we represent according to the nature and the multiplicity of the elements by $(g_\infty)_2$ and $(\varepsilon_\infty)_1$. Beside the general case, where $\varepsilon_\infty'^{(2)}$ has in common with V_3^3 three points not situated on a right line, the particularity may arise that $\varepsilon_\infty'^{(2)}$ has a line in common with one of the planes ε_∞ of $(\varepsilon_\infty)_1$ or coincides with one of those planes; to this answer the particularities that two of three generally different angles of position or all three of them become equal to each other. In the last case of the three equal angles of position, to which we restrict ourselves here, there is between the two systems of incidence this connection, that the plane passing through an arbitrarily chosen point O at finite distance and an arbitrary line g_∞ of $(g_\infty)_2$ is a plane of position for the pair of spaces connecting O with each of two arbitrarily chosen planes ε_∞ of $(\varepsilon_\infty)_1$. If namely we make on each of the lines g_∞ of $(g_\infty)_2$ those points to correspond to each other which are conjugate to each other in the involution determined by the pairs of points of intersection of that line with the planes $\varepsilon_\infty^{(1)}, \varepsilon_\infty'^{(1)}$ and $\varepsilon_\infty^{(2)}, \varepsilon_\infty'^{(2)}$, then between the planes ε_∞ of $(\varepsilon_\infty)_1$ is formed a quadratic involution, from which ensues that the plane ε_∞' normally conjugate to the plane ε_∞ of the variety V_3^3 lies likewise in V_3^3 , etc.

The two double planes $\varepsilon_i, \varepsilon_j$ of the involution $(\varepsilon_\infty, \varepsilon'_\infty)$ form part of the imaginary hypersphere B_4^2 with four dimensions at infinite distance common to all hyperspheres B_5^2 with five dimensions of S_6 . So the section V_2^6 of V_3^2 and B_4^2 consists of these two planes and a V_2^4 which must now necessarily be the locus of the transversals g_∞ of $(g_\infty)_2$ lying entirely on B_4^2 . Whilst as is known the lines g_∞ resting on any arbitrary right line of ε_∞ form a surface

of order two, the locus of the lines g_∞ resting on the conic of section of ε_∞ and B_4^2 is a V_2^4 .

4. If finally in S_{2n} two spaces S_n are taken arbitrarily, these form with each other, as was mentioned above, in their point of intersection O in general n angles differing from each other and the line at infinite distance of the plane of position of each of those angles in the space at infinite distance S_{2n-1} of S_{2n} intersects again four spaces S_{n-1} , the spaces at infinite distance $S_{n-1}^{(1)}$, $S_{n-1}'^{(2)}$

of the two given spaces $S_n^{(1)}$, $S_n^{(2)}$ and the spaces $S_{n-1}'^{(1)}$, $S_{n-1}'^{(2)}$ normally conjugate to these. If now the special case presents itself that each right line cutting three of the four spaces $S_{n-1}^{(1)}$, $S_{n-1}^{(2)}$, $S_{n-1}'^{(1)}$, $S_{n-1}'^{(2)}$ also cuts the fourth, the n angles of position are mutually alike and the locus of the n -fold infinite system $(g_\infty)_n$ of the lines g_∞ at infinite distance of the planes of position is a variety V_n^n of order n with n dimensions, appearing likewise as the locus of a simple infinite number of spaces S_{n-1} , i.e. in the form of $(S_{n-1})_1$, namely of the spaces S_{n-1} , determining with $S_{n-1}^{(1)}$, $S_{n-1}^{(2)}$, $S_{n-1}'^{(1)}$ and now also with $S_{n-1}'^{(2)}$ on the lines g_∞ of $(g_\infty)_n$ mutually projective series of points. In that case a plane connecting an arbitrary point O at finite distance with a line g_∞ of $(g_\infty)_n$ is always a plane of position of each two of the spaces S_n connecting O with spaces S_{n-1} of $(S_{n-1})_1$.

As is immediately evident, in this special case the section Γ_{n-2}^{2n} of Γ_n^n with the hypersphere S_{n-1}^2 with $2n-2$ dimensions common to all hyperspheres B_{2n-1}^2 of S_{2n} breaks up into the two double spaces $S_{n-1}^{(i)}$, $S_{n-1}^{(j)}$ of the involution of the spaces S_{n-1} , S_{n-1}' of $(S_{n-1})_1$ normally conjugate to each other and into a $V_{n-1}^{2(n-1)}$, locus of the lines g_∞ of $(g_\infty)_n$, lying entirely on B_{2n-1}^2 .

Physiology. — "*The principle of entropy in physiology.*" By Dr. J. W. LANGELAAN. 3^d part. (Communicated by Prof. T. PLACE).

All investigations made with the intention of testing the law of FECHNER at the experiment, have proved, that this law is only satisfied within a small interval and within that interval only by approximation.

In order to find out the causes of these deviations, I have tried to deduce the law of FECHNER (considered as a physiological law) from a general physical principle. It has appeared from this deduction that this formula rests on very special premises, and that the circumstances assumed in these premises, are never realized in nature.

In a series of experiments I have tried to fulfil as accurately as possible the conditions required by this law according to its deduction. To this purpose the spinal cord of a frog ¹⁾ was cut between the cranium and first vertebra; then the whole frog, with exception of the hind leg which was used for the experiment, was wrapped up in wads and fastened to a glass rod. The leg hung down in a wide vessel which could contain about 600 ccm. of fluid. In the sole of the foot a hook was put and a horsehair was attached to this hook, which passed outside through a very small opening in the bottom of the vessel. This horsehair was fixed to the arm of a length-recorder.

The small opening through which the hair passed was filled up with vaseline; this prevented almost perfectly the fluid to drip out, while the friction experienced by the horsehair was very slight. By suspending a weight to the length-recorder the leg was charged with 15 grams. Then the vessel was filled with 350 ccm. of water, and the leg immersed till the knee. To the stand bearing the glass and the frog, a clamp was fixed bearing a burette. This burette contained a solution of oxalic acid in distilled water. By opening the tap this solution flowed into the water in which the leg hung. A bent stirrer always kept in slow motion (but which did not touch the leg), caused the acid to be thoroughly mixed with the fluid. Then so much acid was slowly added to the liquid till the leg began to contract. The vertical motion of the leg, three times magnified, was registered on a slowly rotating cylindre by the length-recorder. In order to prevent too large excursions, the length-recorder struck against a piece of cork, so that the contraction in the beginning took place isotonicly, at the end isometrically.

After the leg had returned to rest, we waited about 5 minutes and

¹⁾ Small male specimens of *Rana esculenta* proved to be the most suitable for the experiment.

then again so much acid was added, till a new group of reflex-contractions appeared. In these experiments the acid in the burette contained 40 grains of oxalic acid per liter solution. As a measure of the stimulus in physical units the concentration of the solution, in which the leg was immersed, was chosen. The concentration is defined as the proportion between the quantities of oxalic acid and water, while as the unity of weight the molecular weight was chosen (126 for oxalic acid, 18 for water).

The result of the experiments was given in a table in the following way. The first column gives the concentration of the solution in the vessel, just at the moment the leg begins to show a group of reflex-contractions. The second column contains the increment, which the concentration in the vessel must undergo to produce again a set of reflex-contractions. The third column gives the relation between this quantity and the absolute value of the concentration at the moment that the reflex-contractions appear. This column contains therefore the quotient of WEBER.

Let us now consider in how far this experiment satisfies the conditions put by the formula. The researches of ECKHARD, KOSCHEWNIKOFF, C. MEYER and SHERRINGTON have proved, that the same spinal segments which innervate the skin of the hind leg, supply also the muscles of the leg with nerves. If we have cut the spinal cord at the upper end and have therefore annulled the influence of the higher centra, we have in the hind leg a segmental primary reflex-apparatus. The receptive organs of this reflex-apparatus lay in the skin, while the muscle forms the transformer. Adopting the simple law of distribution, I record only the mechanical effect. In this respect the experiment fulfils the required conditions.

The interpretation of the mechanical effect is very difficult as the new state of equilibrium is not reached at once, but only after oscillating round this new state. It is therefore hard to say what part of the total effect must be considered as the quantity ΔE of the formula. Fig. I is the reproduction of a typical tracing. After the reflex-apparatus is in perfect rest, the tap of the burette is opened at the moment indicated in the curve by a couple of vertical small lines on the base line and oxalic acid is slowly added under continuous stirring. At the moment that the first contraction appears, the tap of the burette is closed and no more acid is added. At this moment the increase of concentration amounted to 3.2×10^{-5} the initial concentration being 15.9×10^{-5} . The curve represents the mechanical effect, following upon this increase of the concentration of the acid in the vessel. This effect consists of a group of great contractions, followed

by some smaller ones of decreasing size. If we should be at first inclined to consider this group of large contractions as the mechanical effect corresponding to the quantity ΔE of the formula, this conception offers many difficulties when the mechanical effect assumes a form as is represented by the curve which is reproduced by fig. II. In consequence of a small increase of concentration we do not see a definite effect appear, not even partly defined, but the reflex-apparatus comes in rythmical contraction. Where in the first case the resistances in the chemical system are such that the oscillations rapidly die away, and the new state is reached after a few oscillations, these resistances in the second case are so small, that once the equilibrium disturbed, the system remains oscillating round its new state of equilibrium. This oscillation documents itself as a rythmical mechanical effect. If the rate of decay of these oscillations is very small, these rythmical

TABLE I. (Fig. V.)

No 4. (12 9. 01.)		
Conc.	Δ Conc.	$\frac{\Delta \text{ Conc.}}{\text{Conc.}}$
0.0×10^{-5}	10.1×10^{-5}	
10.1	2.8	0.218
12.9	3.4	0.209
16.3	4.0	0.196
20.3	4.1	0.167
24.4	4.3	0.150
28.7	4.9	0.147
33.6	4.8	0.123
38.4	10.7	0.248
49.1	20.8	0.298
69.9	10.7	0.133
80.6		

Section of the medulla 10 A.M.
beginning of the experiment 11.15 A.M.
Temp. 13.5 C.

TABLE II. (Fig. VI.)

No 35. (25. 12. 01.)		
Conc.	Δ Conc.	$\frac{\Delta \text{ Conc.}}{\text{Conc.}}$
0.0×10^{-5}	26.6×10^{-5}	
26.6	5.0	0.158
31.6	2.9	0.086?
34.5	3.2	0.085
37.7	2.3	0.058
40.0	2.0	0.047
42.0	1.6	0.037
43.6	2.7	0.059
46.3	3.5	0.069
49.8	5.4	0.098
55.2	10.8	0.164
66.0	19.3	0.226
85.3		

Section of the medulla 10.35 A.M.
beginning of the experiment 12.40 P.M.
Temp. 13 C.

contractions can last for several hours and often with great regularity ¹⁾. Under these circumstances, however, ΔE is no more a determined quantity and the experiment cannot fulfil the condition of the formula, that ΔE be a constant quantity in the successive determinations. If we only use those experiments, in which the resistances are pretty considerable, and the new state of equilibrium is reached after a few oscillations, ΔE fulfils the condition, that it represents a small quantity in successive determinations. The experiment does not allow another more definite conception of this quantity.

By the addition of acid from the burette to the liquid in which the leg is immersed, the level of the liquid rises, and the stimulated surface increases. So the experiment does not fulfil the condition of the formula in this respect either.

TABLE III.

No 21. (7. 12. 01.)		
Conc.	Δ Conc.	$\frac{\Delta \text{ Conc.}}{\text{Conc}}$
0.0×10^{-5}	3.6×10^{-5}	
3.6	1.7	0.327
5.3	1.4	0.203
6.7	2.1	0.236
8.8	3.6	0.292
12.4	6.3	0.339
18.7	10.5	0.359
29.2	12.4	0.297
41.6	8.7	0.173
50.3	26.0	0.271
76.3		

Section of the medulla 10.15 A.M.
beginning of the experiment 12.56 P.M.
Temp. 15 C.

TABLE IV. (Fig VII.)

No. 14. (21. 9. 01.)		
Conc.	Δ Conc.	$\frac{\Delta \text{ Conc.}}{\text{Conc.}}$
0.0×10^{-5}	15.9×10^{-5}	
15.9	3.2	0.168
19.1	4.5	0.192
23.6	7.3	0.235
30.9	8.0	0.207
38.9	4.3	0.098
43.2	3.8	0.082
47.0	19.9	0.297
66.9	27.6	0.292
94.5	16.8	0.151
111.3	15.3	0.121
126.6		

Section of the medulla 10 P.M. 20.9,
beginning of the exper. 12.1 P.M. 21.9
Temp. 16.5 C.

¹⁾ It seems to me that the heart is in this condition, and it would be worth while to repeat many experiments from the physiology of the heart on this rhythmically acting reflex-apparatus.

Similar experiments as described by me, were performed by WINKLER and VAN WAYENBURG some years before. The method followed by them, which slightly deviated from mine, enabled them to extend the experiment only over a small interval of variation of concentration. They concluded for this small interval, that the reflex-apparatus of the frog follows the law of FECHNER¹⁾. In the experiments communicated by them slight deviations from this law proved to occur and it was with the purpose of learning something about these deviations, that I repeated these experiments extended over a greater interval. Table I, II, III and IV represent four of these experiments. If we take R as the value of the stimulus in physical measure (i. e. the concentration of the solution of the acid in which the leg is immersed) and if we take ΔR as the value of the increment of this stimulus which is required to call forth a change in the system, the quotient $\frac{\Delta R}{R}$ is not constant, but in general a function of R .

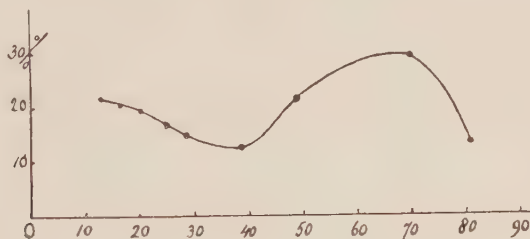


Fig. V (table I, exper. 4).

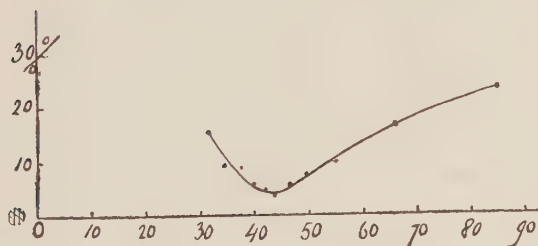


Fig. VI (table II, exper. 35).

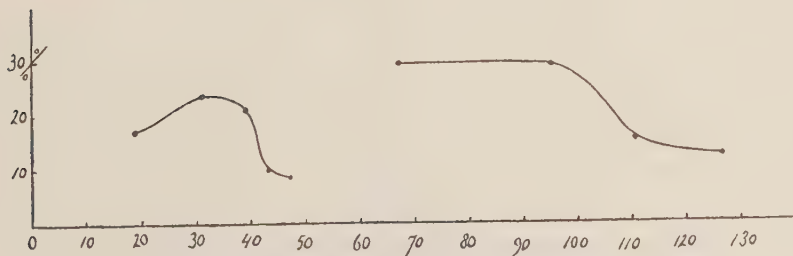


Fig. VII (table IV, exper. 14).

¹⁾ VAN WAYENBURG, Dissertation 1897. pag. 117.

Fig. V, VI, and VII are the graphical representation of Table I, II and IV. In this graphical representation I have considered the amount of water as constant (10^3 unities of weight) and put as abscissae the number of solved unities of weight of the acid. The relative increases of the concentration, in percents, have been chosen as ordinates. The points, representing successive determinations, are connected by a curve. The graphical representation of the result of the experiment by a continuous curve is only an approximation, remaining in the same course of thoughts as that, which has led us to represent the phenomenon analytically by a continuous function.

If the law of FECHNER was satisfied, the line representing graphically the quotient $\frac{\Delta R}{R}$ as function of R , would be a straight one. But

instead the experiment furnishes a curved line. In order to elucidate the form of this curve further, fig. V is given, which is the graphical representation of an experiment, where the first descending branch is determined by as large a number of observations as is possible. Fig. VI shows a reduction in the extent of the first descending branch and this enables us to determine the ascending branch by a greater number of observations. In the experiment represented by fig. VII this reduction of the first descending branch is so considerable, that it no more appears in the experiment; this makes it possible to determine the top of the ascending branch and the descending branch following on it. The whole course of the second descending branch cannot be given, as always a discontinuity occurs at a point which seems to be near a second minimum. After this discontinuity a new period sets in, and as far as it is possible to follow this new period, it appears to be considerably greater, whereas

the oscillation which the value of the quotient $\frac{\Delta R}{R}$ shows in this period, seems to be relatively smaller. For a skin-muscle reflex-apparatus the quotient $\frac{\Delta R}{R}$ must therefore be considered as a periodic

function of R . If we inquire what is the signification of this discontinuity, it seems that only those variables, which are the representation of the independently variable components of the chemical system, can be able to show discontinuities. This brings about a change in the nature of the system and this must be attended by a discontinuous variation of the quantity R , which occurs in formula I of the second communication. The experiment communicated by MASSART ¹⁾ seems

¹⁾ Bull. Acad. royale de Belgique 3me Série, T. 16, 1888, pag. 590.

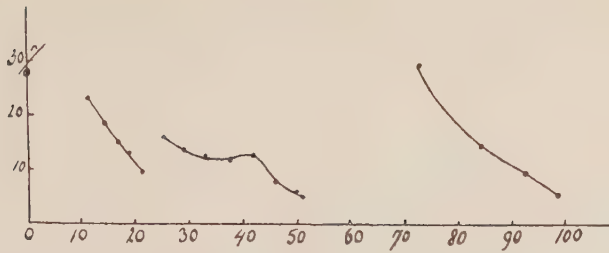


Fig. VIII (table V, exper. 25).

TABLE V. (Fig. VIII.)

No. 25. (11. 12. 01.)		
Conc.	Δ Conc.	$\frac{\Delta \text{ Conc.}}{\text{Conc.}}$
0.0×10^{-5}	8.8×10^{-5}	
8.8	2.7	0.232
11.5	2.7	0.187
14.2	2.6	0.156
16.8	2.4	0.129
19.2	2.0	0.093
21.2	4.0	0.160
25.2	4.0	0.136
29.2	4.1	0.123
33.3	4.5	0.120
37.8	4.3	0.123
42.1	3.8	0.079
45.9	3.0	0.061
48.9	2.5	0.050
51.4	21.0	0.289
72.4	11.8	0.144
84.2	7.1	0.097
93.3	5.0	0.051
98.3		

Section of the medulla 8.30 A.M.
beginning of the experiment 12.5 P.M.
Temp. 13 C.

to show the same phenomenon. Another phenomenon, which sometimes occurred in my experiments, was the dividing of a period into several parts. Fig. VIII (table V) is the graphical representation of such an experiment.

As far as my experiments go, this small discontinuity can appear at every moment in a given period, followed by the outset of a new period.

If we compare these results obtained by the primary reflex-apparatus with those of experimental psychology, they appear to concord in many points. As appears from the critical summary of FOUCAULT¹⁾ also there a variable quantity showing a minimum is found for the

quotient $\frac{\Delta R}{R}$ in most cases. The shape of the curve representing the quotient $\frac{\Delta R}{R}$ as function of R , makes us suppose, that the experimental

psychology has seen only part of a large period. By the dividing of a period into several parts, the quotient $\frac{\Delta R}{R}$ seems to show multiple minima and this occurs also in some experiments of the experimental psychology. Hence there is agreement in these respects between the results of the psychological and the physiological experiment.

With regard to the mechanical effect I have pointed out, that this is greatly dependent on the rate of decay of the oscillations of the system. The rapidity of this decay is determined by the passive resistances in the chemical system. If these passive resistances are slight, a small increase of R will be sufficient to call forth a change in the system. Therefore the value of the quotient $\frac{\Delta R}{R}$, which is a measure of the value of these passive resistances, will determine the rapidity of the decay of these oscillations.

In correspondence with this the experiment shows that the height and the number of the elevations in every successive determination increases with decrease of the value of the quotient $\frac{\Delta R}{R}$. Fig. III (table II) observation 2, 3, 4, 5 shows this clearly. At the 5th observation the resistances are so slight, that the system continues to oscillate for several seconds. Observation 8 and 10 show this same phenomenon at a higher value of R , in the same series of observations. If we compare, however, observation 8 with observation 5, in which two observations the value of the quotient $\frac{\Delta R}{R}$ is almost the same, and

¹⁾ M. FOUCAULT. La psychophysique, 1901.

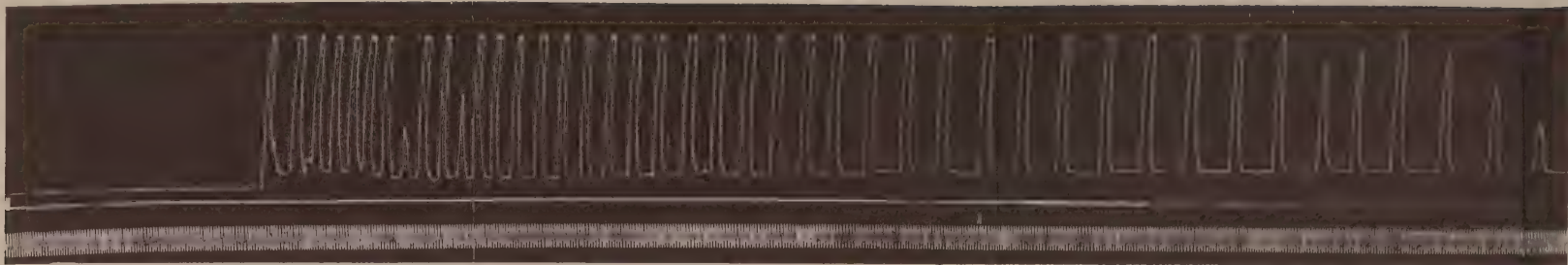


Fig. II. (Exp. N^o. 24.) Tuningfork 2 vibrations per second.

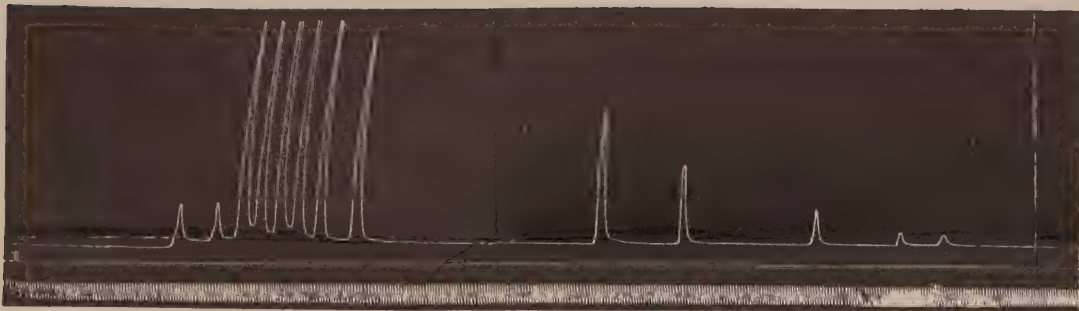
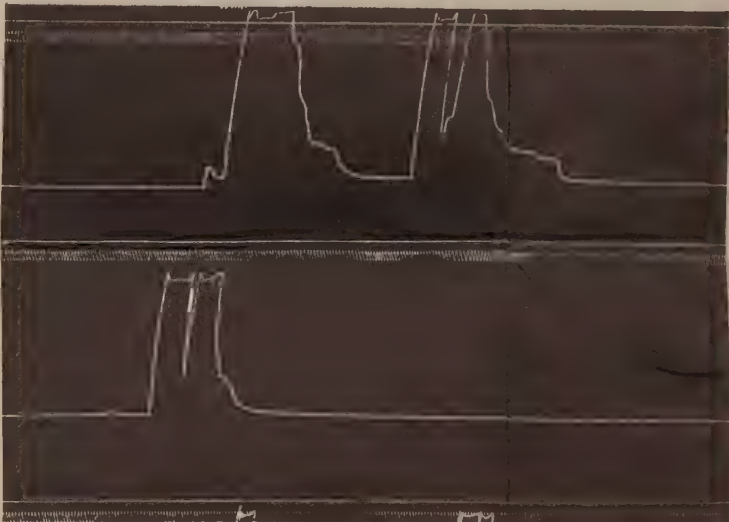


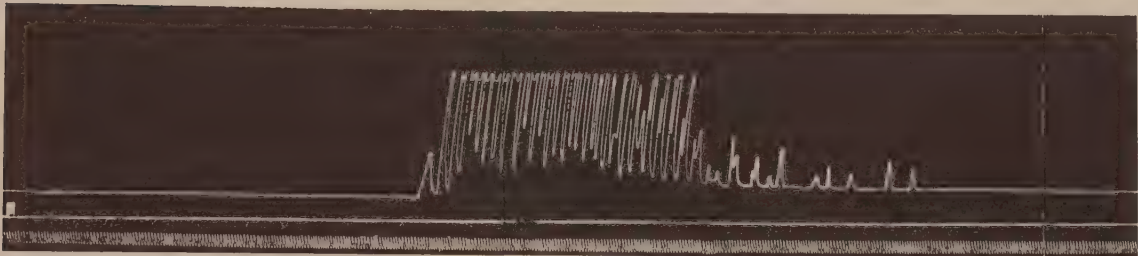
Fig. I. (Exp. N^o. 14.) Tuningfork 2 vibrations per second.

$$\frac{\Delta R}{R} = 0.168$$
$$R = 19.1 \times 10^{-5}$$



$$R = 171 \times 10^{-5}$$
$$\frac{\Delta R}{R} = 0.206$$

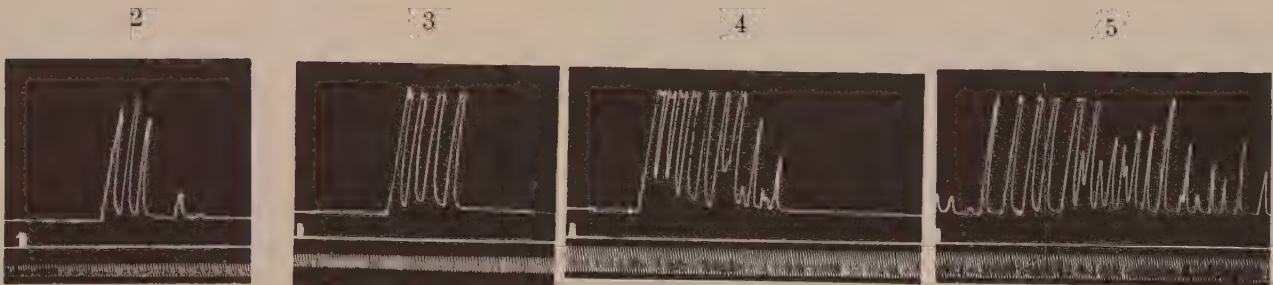
$$R = 96.8 \times 10^{-5}$$
$$\frac{\Delta R}{R} = 0.234$$



$$R = 26.6 \times 10^{-5}$$



$$R = 195.4 \times 10^{-5}$$
$$\frac{\Delta R}{R} = 0.125$$

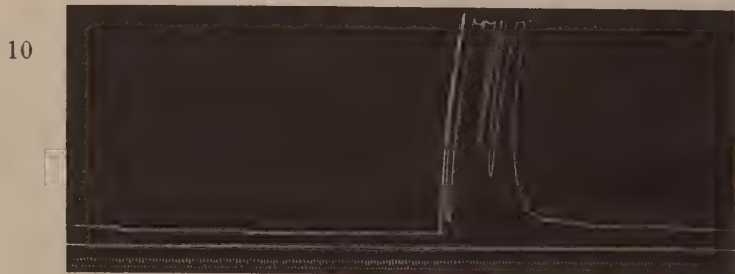


$$R = 31.6 \times 10^{-5}$$
$$\frac{\Delta R}{R} = 0.158$$

$$R = 34.5 \times 10^{-5}$$
$$\frac{\Delta R}{R} = 0.086?$$

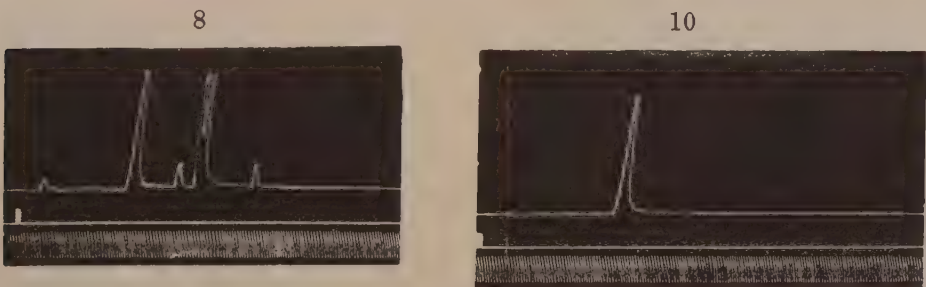
$$R = 37.7 \times 10^{-5}$$
$$\frac{\Delta R}{R} = 0.085$$

$$R = 40.0 \times 10^{-5}$$
$$\frac{\Delta R}{R} = 0.058$$



$$R = 413.9 \times 10^{-5}$$
$$\frac{\Delta R}{R} = 0.093$$

Fig. IV. (Exp. N^o. 50.) Tuningfork 2 vibrations per second.



$$R = 46.3 \times 10^{-5}$$
$$\frac{\Delta R}{R} = 0.059$$

$$R = 55.2 \times 10^{-5}$$
$$\frac{\Delta R}{R} = 0.098$$

Fig. III. (Exp. N^o. 35.) Tuningfork 2 vibrations per second.

also observation 10 with observations 3 and 4, it appears, that in the second place the rate of decay is dependent on the absolute value of R . Supported by these and more similar observations we may say that the rapidity of the decay of the oscillations increases with increasing value of R and with increasing value of the quotient $\frac{\Delta R}{R}$.

In this we have to keep in view, that the first observation always occupies a special place; for this observation ΔR is always very large, and though the method followed does not enable us to determine the quotient $\frac{\Delta R}{R}$ for this observation, this quotient is probably also very great. Notwithstanding this we always see that the rate of decay is very slight and from this we should have to conclude, that the influence of the absolute value of R on the rapidity of this decay is preponderant in the beginning.

The same experiments which I have described for the frog whose spinal cord is cut through, can also be performed with perfectly intact frogs. For this it is necessary to wrap up the whole animal carefully in wads with exception of the hind leg which is used for the experiment. If we take care to avoid tactile and auditory stimuli, the frog remains quiet during the experiment also under these circumstances¹⁾. In this case the result of the experiment is the same as that of the preceding one.

Fig. IX (table VI) is the graphical representation of an experiment.

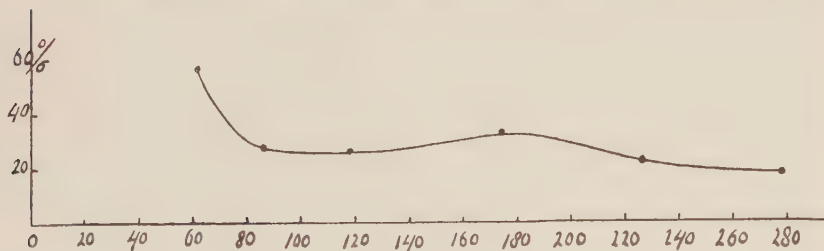


Fig. IX (Table VI, exper. 46).

If the first period is small, it is possible to see also here a part of a second period appear (Fig. X, table VII). This second period seems also greater than the first, while the oscillation, which the value of the quotient $\frac{\Delta R}{R}$ shows in this period, seems relatively to be smaller.

¹⁾ In these experiments the solution of acid in the burette contained 80 grams of oxalic acid per liter solution.

TABLE VI. (Fig. IX.)

No. 46. (18. 1. 02.)		
Conc.	Δ Conc.	$\frac{\Delta \text{ Conc.}}{\text{Conc.}}$
0.0×10^{-5}	26.9×10^{-5}	
26.9	34.6	0.562
61.5	24.1	0.282
85.6	32.1	0.273
117.7	55.9	0.322
173.6	52.3	0.231
225.9	52.2	0.187
278.1		

Medulla intact. Beginning of the experiment 11.46 A.M. Temp. 13.5 C.

TABLE VII. (Fig. X.)

No 50. (26. 1. 02.)		
Conc.	Δ Conc.	$\frac{\Delta \text{ Conc.}}{\text{Conc.}}$
0.0×10^{-5}	29.3×10^{-5}	
29.3	44.9	0.605
74.2	22.6	0.234
96.8	39.0	0.546
135.8	35.2	0.206
171.0	24.4	0.125
195.4	53.0	0.213
248.4	71.6	0.224
320.0	55.4	0.148
375.4	38.5	0.103
413.9		

Medulla intact. Beginning of the experiment 3.0 P.M. Temp. 41.5 C.

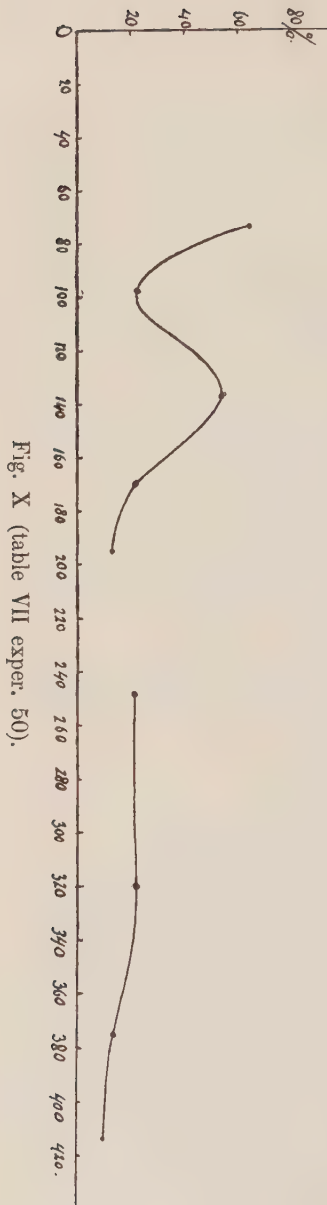


Fig. X (table VII exper. 50).

The number of my experiments in which a second period appears, is, however, not great. Therefore we may say also in this case, that the quotient $\frac{\Delta R}{R}$ is probably to be considered as a periodical function

of R . The value of the quotient $\frac{\Delta R}{R}$, however, is in these experiments considerably greater than in the preceding experiments, while in concordance with this the rapidity of the decay of the oscillations of the system is also greater.

Figure IV (table VII) which is the reproduction of four observations from the same series, shows this clearly; the new state of equilibrium is reached after a few oscillations. If we compare observation 3, 5 and 6, the system proves to be a periodical one, at the third observation; at observation 5 and 6 the rapidity of the decay decreases with decreasing value of the quotient $\frac{\Delta R}{R}$. At the tenth obser-

vation, where the quotient $\frac{\Delta R}{R}$ shows a very low value, the rapidity of the decay is very small notwithstanding the high value of R . If we summarize these differences briefly, we conclude that in consequence of the high section of the spinal cord, the passive resistances in the chemical system of the skin-muscle reflex-apparatus considerably decrease. On account of clinical observation chiefly regarding the plantar-reflex, it seems to me, that we have to deal here with a very general phenomenon occurring always where there is a wasting of systems. In this case the rapidity of the decay of the oscillations of the system is very small in consequence of the decrease of the passive resistances in the chemical system. It is obvious that a good motor function can only exist, when the rapidity of the decay is so great, that the system is almost aperiodic. The motor disturbances, which occur in multiple sclérosis, in locomotor ataxy and many other diseases of the nervous system seems to be partly due to the decreasing resistances in the chemical system of the reflex arc.

If the system is perfectly aperiodic, then the quantity ΔE is a perfectly determined quantity. This condition must also be fulfilled by the systems, to which the experimental psychology extends its experiments; if this condition is not satisfied, then the effect is a not determined quantity as in the physiological experiment.

Astronomy. — "*On the yearly periodicity of the rates of the Standard-clock of the observatory at Leiden, HOHWÜ N^r 17.*"
First part. By Dr. E. F. VAN DE SANDE BAKHUYZEN.

I. *Introduction.*

1. When the observatory at Leiden was founded in 1861, it was fitted with a clock made by Mr. A. HOHWÜ of Amsterdam, and by him designated as N^r 17. Accurate investigations of KAISER ¹⁾ soon showed the great regularity of its rate, in which point it was superior to all clocks about which an investigation had so far been published. Since that time it has continually been used as the standard-clock of the observatory and at the present moment its rate is still eminently satisfactory.

The clock was originally mounted in the transit-room of the observatory on a brick pier which rests on the foundations of the meridian-circle. The stability of the mounting thus left nothing to be desired. On the other hand the temperature at this place was rather variable, showing very clearly a daily period; moreover entirely irregular changes of temperature were often caused by the opening and closing of the shutters.

From 1861 the clock has been going regularly until 1874, without being touched during this time except for the purpose of winding once a week. On the 17th of June of the latter year however it stopped spontaneously, after having shown for about a month a particular irregularity.

As the intention existed already to make considerable changes as well in the transit-room as in the meridian-circle, it was thought best to defer a thorough cleaning and overhauling of the clock till the time of these alterations. Accordingly the clock was then only provisorily cleaned, and was set going again after a few days.

The intended alterations were made in the second half of 1876 and the beginning of 1877, and in June of that year everything was again in working order, and also the clock HOHWÜ 17 was mounted again.

Though Prof. H. G. VAN DE SANDE BAKHUYZEN did consider the possibility of removing it to a better position, out of the transit-room,

¹⁾ F. KAISER, Onderzoekingen omtrent den gang van het hoofduurwerk der sterrenwacht te Leiden, de pendule HOHWÜ N^o. 17. *Versl. en Meded. K. Akad. Amsterdam D. XVII*, 1865.

F. KAISER, Untersuchungen über den Gang der Hauptuhr der Sternwarte in Leiden, HOHWÜ N^o. 17. *Astr. Nachr.* N^o. 1502.

this gave rise to too many difficulties at the time, and it was only tried to diminish the variations of temperature by making a second wooden case round the clock.¹⁾

In the meantime the chronographic method had been generally adopted at the observatory for the meridian observations. Now it had been shown repeatedly that the introduction of an electrical contact in a clock diminishes the regularity of its rate, and on the other hand we had found that the comparison of two clocks could be effected with extreme accuracy by means of signals given by hand²⁾. Accordingly the clock HOHWÜ was not connected with the chronograph, but the clock by KNOBLICH was used for this purpose.

On the 26th of November 1877 the clock was stopped for a short time in order more completely to adjust its beats; since that date however it has been going uninterruptedly until August 1898. At that time the clock was again dismounted at the occasion offered by alterations in the transit-room, and cleaned and overhauled by Mr. HOHWÜ,

In December 1898 the clock was remounted, and this time the former plan of removing it from the transit-room was carried out, and it was fixed to the pier of the 10 inch refractor. In order better to secure a constant temperature, Prof. H. G. VAN DE SANDE BAKHUYZEN resolved to have a niche cut out from this pier in the large hall of the observatory, and to place the clock in this niche.

The clock HOHWÜ N° 17 has now been in its new place for over three years. It is still enclosed in two wooden cases, and the niche itself is closed by a glass door. We may remark already at this place that by this arrangement the aim of excluding rapid variations of temperature has been attained in a very perfect manner.

2. In 1887 Mr. WILTERDINK investigated for a special purpose the rate of the clock HOHWÜ 17 during the period 1886 January to 1887 July. It then appeared that after reduction for temperature and barometer the mean rates for the summer- and the winter-half-years were in very satisfactory agreement, while on the other

¹⁾ At the same time a small mirror was attached to the pendulum-bob, to permit more accurate determinations of the amplitude of oscillation. See: H. G. VAN DE SANDE BAKHUYZEN, *Verslag van den staat der sterrenwacht te Leiden 1876—1877*, page 12.

²⁾ From series of signals given by the two observers WILTERDINK and E. F. VAN DE SANDE BAKHUYZEN immediately after each other, on a great number of days, the Mean Error of the result of a series of about 24 signals, (including the variation of the constant error during an interval of about a month) is found to be $\pm 0^s.0077$.

hand a very marked systematic difference existed between the means for the half-years January—June and July—December.

Mr. WILTERDINK found

	Obs.—Comp.
1886 January—June	+ 0 ^s .045
July—December	— 0 .03
1887 January—June	+ 0 .035.

Consequently, when in 1890 I undertook the definitive discussion of the time-determinations and clock-rates for the period 1877—1882, it appeared desirable to me to investigate whether a similar phenomenon would again show itself. I then found that the years 1878—1882 (before May 1878 the rate was not yet sufficiently regular) were in this respect entirely similar to 1886—87, and, investigating the phenomenon more closely, I moreover found that the rates, after correction for temperature, still showed a yearly periodicity which accordingly had its maxima in the months of equal temperatures April and October and the amplitude of which was about 0^s.10.

I then continued my investigation (the results of which were briefly published in the "*Verslag van den staat der sterrenwacht te Leiden 1889—1890*," pages 14—15) in the same direction and included on the one side the years 1882—90, using provisional results of the time-determinations, and on the other side the years 1862—1864, using the results of KAISER's investigation in *Astr. Nachr.* 1502. For these two periods I also found the same unexplained inequality.

After 1890 this investigation was abandoned for the time being, and it was only taken up again last year. In the mean time the clock had been removed to its new position, and it now appeared that, notwithstanding the fact that the changes of temperature had become much more gradual, still the yearly periodicity of the rate showed itself in the same way as before, and its deviation from the yearly periodicity of the temperature was certainly not less evident¹⁾.

It became thus evident that there was no question of accidental circumstances, which could be altered by cleaning the clock, nor of such conditions as depend on the special nature of the changes of temperature to which the clock is subjected, but that the cause of the phenomenon must lie deeper.

It therefore appeared desirable to subject the way in which it showed itself in the three periods (*viz.*: before and after the cleaning

¹⁾ See also "*Verslag van den staat der sterrenwacht te Leiden 1898—1900* pages 12—13.

of 1877, and after the cleaning and removal of 1898) to a new investigation which had to embrace the whole of these periods. The results of this investigation are given in the present paper.

I have confined myself to such results as could be derived from the mean daily rates during periods of about a month. Thus it was not necessary that the time-determinations on which the investigation is based were discussed with the utmost accuracy. In this way I investigated successively the three periods, 1877—1898, 1862—1874 and 1899—1902. The results for these three periods will be communicated in this order. Then the observed amplitudes of the period 1877—1898 will be investigated, so far as their yearly periodicity is concerned, and finally the several results will be compared with each other.

As a consequence of the restriction of the investigation to the monthly means, the question is considered from one point of view only. In the mean time however Mr. WEEDER has definitively discussed all the time-determinations from 1882—1898, and has undertaken investigations about the rates of the clock during shorter periods. It is to be expected that, when these investigations will be completed, the comparison of his results with mine will also throw more light on the phenomenon which is here treated.

Very recently, while my investigation was already nearly completed, I had occasion more closely to study the computations which KAISER made about the clock HOHWÜ 17 during the last years of his life, and which are preserved in manuscript at the observatory. I then found that as early as 1870 his attention had been drawn to this particular yearly inequality as to a remarkable phenomenon. Among the papers I found a summary of monthly means of rates, corrected for barometer and temperature, from which mean results had been formed by combining the corresponding months of the years 1862—1870. These means show clearly a periodicity having its maxima in May and October, and a total amplitude of 0^h.09. Further I found means for the half-years February—July and August—January for each of the years 1863 to 1870. The differences between the two half-years vary between $+0^{\text{s}}.026$ and $+0^{\text{s}}.048$ and KAISER adds the remark that the only difference between the two half-years is that in one of them the temperature is, in the mean, rising, while in the other it is falling.

II. *The period 1877—1898.*

3. The clock-rates which were taken as the basis of the investigation were, for the period 1877—March 1882, derived from the

definitive discussion of the time-determinations during that period. For the following years they were taken from the provisional results which had been computed immediately after the observations, Mr. WEEDER's results being not yet completed last year. I only applied small corrections in a few cases for the personal differences between the observers, which have become better known since the provisional computations were made. I always used time-determinations as near as possible to the beginning of each month.

The mean temperatures and barometerreadings required for the investigation were derived in the following way.

The temperature was read on two thermometers suspended in the clock-case, one at the level of the upper part of the pendulum rod the other at the level of the pendulum bob. These thermometers were read five times a day viz. at 8 a.m., noon, 4 p.m., 8 p.m. and midnight. The scales were REAUMUR's and were divided into full degrees.

We will first investigate the relation between the results given by the two thermometers. The readings of the years 1878, 1879, 1884 and 1885 were discussed for this purpose. In the following table the monthly means of the differences between the two thermometers are given for each of these four years, after application of the index-corrections. The differences are taken in the sense upper thermometer-lower thermometer. The last column gives the means of the four years.

	1878	1879	1884	1885	Mean
January	+ 0.16	+ 0.12	+ 0.19	+ 0.16	+ 0.16
February ...	+ 0.18	+ 0.16	+ 0.19	+ 0.21	+ 0.18
March	+ 0.20	+ 0.21	+ 0.22	+ 0.20	+ 0.21
April	+ 0.33	+ 0.25	+ 0.24	+ 0.27	+ 0.27
May	+ 0.28	+ 0.29	+ 0.27	+ 0.24	+ 0.27
June	+ 0.29	+ 0.26	+ 0.26	+ 0.29	+ 0.28
July	+ 0.26	+ 0.24	+ 0.25	+ 0.28	+ 0.26
August	+ 0.22	+ 0.22	+ 0.27	+ 0.25	+ 0.24
September ..	+ 0.21	+ 0.20	+ 0.22	+ 0.22	+ 0.21
October	+ 0.18	+ 0.19	+ 0.20	+ 0.19	+ 0.19
November...	+ 0.16	+ 0.18	+ 0.20	+ 0.18	+ 0.18
December ...	+ 0.13	+ 0.18	+ 0.18	+ 0.17	+ 0.16

There appears to be a constant difference of about + 0°.2 between

the two temperatures. There also seems to be a small yearly inequality. We will return later on to these small differences between the separate months, and investigate the influence which they can have had on the rate of the clock, *if they are real*.

For the rest of the investigation the readings of the upper thermometer were used exclusively. I first formed daily means¹⁾ — the day being reckoned from midnight to midnight — and then means for the periods of about one month. The index-correction, which may be taken constant and equal to $-0^{\circ}.6$ for the whole period, was not applied.

Until May 1886 the heights of the barometer were read and reduced in exactly the same way as the temperatures. The readings were made on a mercurial barometer which was suspended in the transit-room from the same pier which also carried the clock. After that time a barograph of RICHARD was used, which was placed on the top of this same pier. Its corrections were determined by comparison with the mercurial barometer²⁾. The daily means were then derived by integration by means of a planimeter of AMSLER.

During the period in question three different cistern barometers were used; in consequence of cleaning and refilling we must however distinguish 7 periods. The corrections for these 7 periods were determined by intercomparisons, by comparisons with simultaneous readings of the barometer of the Meteorological Institute at Utrecht, and finally by comparisons with a "Cistern-syphon" barometer by FUESS, which in 1890 was provided for the observatory, to be used as a Standard barometer. Since however before 1890 no correction had been applied and the neglected corrections amounted to approximately $+0.3$ mm. during the whole period, the readings after 1890 were reduced to: Normal barometer -0.3 mm.

The barometer-readings were not reduced to 0° . This reduction was omitted on purpose, though the errors introduced thereby are by no means negligible (at 760^{mm} the effect of 1° RÉAUM. is 0.15^{mm}). The influence of these errors on the rate of the clock is however nearly completely compensated by the fact that also the influence of the temperature on the rate, which is thus found, differs from the true one. It is here supposed that the temperatures of the barometer has always been equal to that of the pendulum, which condition is

1) The mean was taken of the readings at 12^{h} , 20^{h} , 4^{h} , 12^{h} , giving half weight to the extreme values.

2) A constant correction was taken for each weekly barograph sheet derived from one or two readings of the mercurial barometer daily.

nearly fulfilled in the present case ¹⁾. The only thing that is thus neglected is the difference between the influence of the same temperature on high and on low barometer-readings, which is extremely small.

4. The observed rates were first reduced to 760^{mm} and + 10° R. by means of previously determined values of the coefficients *b* and *c* in the formula:

$$\text{Daily Rate} = a + b(h-760) + c(t-10^{\circ})$$

$$b = + 0^{\circ}.0140$$

$$c = - 0.0268$$

The value of *b* was derived from a rigorous discussion of the period 1877—1882, in which only rates observed under high and low barometric pressure during the same month were compared. This value must be very near to the truth. In all investigations, not only about Hohnw 17, but also about other clocks with similar, or even with different forms of pendulum, barometer-coefficients have always been found of nearly the same amount, and it is not probable that its value would vary with the time for one and the same clock.

The value $b = + 0^{\circ}.0140$ has therefore been considered definitive, and I have not attempted to improve it.

The following table gives, for each month from 1877 December to 1898 July, the mean observed daily rate, the mean height of the barometer and the mean temperature, and, in the column headed „Red^d. D. R. I.”, the daily rates reduced to 760^{mm} and + 10° R by the formula given above. The meaning of the two last columns can only be explained later.

¹⁾ See also the particulars given in connection with the investigation of the period 1862—1874.

	Obsd D. R.	Bar.	Temp.	Redd D. R. I	Redd D. R. II	O.—C.
1877 Dec.	+ 0.144 ^s	760.7	+ 4.4	— 0.016 ^s		
1878 Jan.	0.241	66.8	3.9	— 0.016		
Febr.	0.191	67.7	6.1	— 0.020		
March	0.163	59.4	4.9	+ 0.034		
April	0.148	59.5	8.6	0.118		
May	0.106	58.9	11.2	0.152		
June	0.135	62.0	13.7	0.206		
July	0.100	63.4	14.7	0.179		
Aug.	0.038	58.3	14.6	0.184		
Sept.	0.103	62.5	13.0	0.149		
Oct.	0.043	56.9	9.6	0.077		
Nov.	0.062	53.9	5.4	0.025	+ 0.112 ^s	+ 8
Dec.	0.151	54.4	2.5	0.030	097	— 13
1879 Jan.	0.344	61.6	1.6	0.097	144	+ 28
Febr.	0.145	50.9	2.8	0.079	106	— 16
March	0.326	62.2	4.1	0.137	149	+ 21
April	0.151	53.6	6.3	0.144	146	+ 12
May	0.241	62.6	8.3	0.161	161	+ 20
June	0.084	59.5	12.8	0.165	163	+ 16
July	0.024	58.1	13.1	0.133	145	— 8
Aug.	0.039	61.3	14.0	0.127	158	— 1
Sept.	0.061	62.6	12.3	0.088	153	— 12
Oct.	0.139	65.2	9.1	0.042	141	— 30
Nov.	0.301	64.7	+ 4.6	0.092	181	+ 4
Dec.	0.598	69.3	— 0.3	[0.191]		
1880 Jan.	0.529	71.5	+ 1.7	[0.145]	179	— 10
Febr.	0.203	56.6	4.5	0.102	126	— 70
March	0.321	65.6	6.2	0.141	148	— 54
April	0.214	60.8	8.4	0.158	156	— 52
May	0.245	64.1	9.8	0.183	180	— 34
June	0.078	60.2	12.8	0.149	147	— 73
July	0.070	61.0	14.1	0.167	177	— 48

	Obs ^d D. R.	Bar.	Temp.	Red ^d D. R. I	Red ^d D. R. II	O.—C.
1880 Aug.	+ 0.111 ^s	763.3	+ 15.4	+ 0.208 ^s	+ 0.236 ^s	+ 6
Sept.	0.080	62.0	13.8	0.152	214	— 21
Oct.	0.171	60.0	9.1	0.147	246	+ 7
Nov.	0.314	61.2	5.7	0.183	269	+ 27
Dec.	0.279	58.7	5.9	0.189	249	+ 6
1881 Jan.	0.471	58.7	0.4	[0.233]	244	0
Febr.	0.333	58.2	3.1	0.174	201	— 43
March	0.375	59.2	5.1	0.255	265	+ 21
April	0.361	61.1	6.8	0.258	259	+ 16
May	0.306	65.5	10.4	0.239	229	— 13
June	0.226	62.6	12.3	0.250	238	— 2
July	0.180	63.7	15.0	0.264	252	+ 15
Aug.	0.073	58.0	13.4	0.191	209	— 26
Sept.	0.128	62.2	12.0	0.152	208	— 24
Oct.	0.217	61.8	7.4	0.124	231	+ 2
Nov.	0.272	63.0	7.3	0.158	245	+ 19
Dec.	0.322	62.7	4.6	0.140	215	— 8
1882 Jan.	0.479	71.0	4.2	0.170	225	+ 5
Febr.	0.499	71.0	3.5	0.171	213	— 4
March	0.352	64.5	7.0	0.208	219	+ 5
April	0.189	57.7	8.1	0.171	171	— 40
May	0.250	64.6	11.3	0.221	206	— 1
June	0.135	60.7	12.5	0.192	179	— 25
July	0.113	60.9	13.9	0.205	199	— 2
Aug.	0.086	59.7	13.6	0.187	204	+ 7
Sept.	0.105	59.8	12.0	0.162	218	+ 24
Oct.	0.087	59.1	9.3	0.081	178	— 13
Nov.	0.113	54.1	6.1	0.091	185	— 2
Dec.	0.156	54.0	4.3	0.087	164	— 20
1883 Jan.	0.309	60.9	3.5	0.122	181	0
Febr.	0.361	66.4	5.2	0.142	175	— 3
March	0.349	59.8	3.3	0.172	202	+ 27

	Obsd D. R.	Bar.	Temp.	Redd D. R. I	Redd D. R. II	O.—C.
1883 April	+ ^s 0.301	761.1	+ 7.7	+ ^s 0.223	+ ^s 0.225	+ 53
May	0.203	62.4	11.0	0.196	183	+ 15
June	0.134	62.6	13.0	0.178	163	— 2
July	0.053	59.2	13.9	0.169	163	+ 1
Aug.	0.107	63.8	13.9	0.159	174	+ 16
Sept.	0.020	59.5	12.7	0.099	151	— 4
Oct.	0.050	60.0	9.8	0.045	139	— 13
Nov.	0.078	59.0	7.3	0.020	107	— 41
Dec.	0.254	64.2	4.9	0.058	132	— 13
1884 Jan.	0.212	63.1	5.9	0.058	105	— 37
Febr.	0.242	62.1	5.0	0.078	112	— 28
March	0.221	61.0	6.6	0.116	129	— 9
April	0.182	57.3	7.5	0.153	156	+ 18
May	0.205	64.0	11.2	0.181	172	+ 32
June	0.150	63.9	12.1	0.151	147	+ 3
July	0.052	62.7	15.6	0.164	164	+ 15
Aug.	0.087	64.3	15.7	0.179	199	+ 44
Sept.	0.078	63.6	13.8	0.130	187	+ 27
Oct.	0.104	62.4	10.1	0.073	169	+ 4
Nov.	0.323	65.9	5.7	0.125	214	+ 44
Dec.	0.272	59.0	4.4	0.136	203	+ 28
1885 Jan.	0.403	58.8	1.4	[0.190]	212	+ 32
Febr.	0.262	57.2	5.6	0.183	208	+ 23
March	0.399	63.6	4.8	0.210	224	+ 34
April	0.201	56.5	8.7	0.215	212	+ 17
May	0.148	58.1	9.2	0.154	153	— 47
June	0.151	63.6	13.2	0.187	194	— 11
July	0.191	67.7	14.5	0.204	225	+ 15
Aug.	0.117	61.9	12.9	0.168	210	— 4
Sept.	0.097	60.3	11.7	0.138	211	— 8
Oct.	0.031	54.2	8.8	0.080	180	— 43
Nov.	0.305	60.5	4.8	0.159	239	+ 11

	Obs ^d D. R.	Bar.	Temp.	Red ^d D. R. I	Red ^d D. R. II	O.—C.
1885 Dec.	+ 0.422 ^s	765.1	+ 4.3	+ 0.197 ^s	+ 0.251 ^s	+ 19
1886 Jan.	0.313	51.6	2.3	0.225	257	+ 21
Febr.	0.505	63.4	1.5	0.229	244	+ 5
March	0.451	63.6	5.0	0.267	269	+ 26
April	0.353	61.7	7.4	0.259	256	+ 10
May	0.250	61.3	11.4	0.269	268	+ 18
June	0.207	61.6	12.2	0.244	251	— 2
July	0.123	61.4	14.4	0.221	242	— 14
Aug.	0.123	63.0	14.4	0.199	241	— 19
Sept.	0.126	64.1	14.1	0.178	251	— 12
Oct.	0.117	59.1	9.9	0.127	227	— 39
Nov.	0.197	59.0	7.3	0.139	219	— 50
Dec.	0.236	52.1	3.7	[0.178]	215	— 57
1887 Jan.	0.492	63.3	1.4	[0.215]	247	— 27
Febr.	0.595	70.4	2.9	0.259	287	+ 11
March	0.437	62.1	3.8	0.241	257	— 21
April	0.394	62.2	6.6	0.272	281	+ 1
May	0.257	61.3	9.7	0.230	239	— 43
June	0.296	69.0	13.1	0.253	269	— 15
July	0.200	64.4	15.0	0.272	300	+ 14
Aug.	0.195	62.4	14.0	0.268	310	+ 22
Sept.	0.181	61.7	12.3	0.219	273	— 16
Oct.	0.307	61.4	8.0	0.233	294	+ 5
Nov.	0.304	56.4	5.5	0.233	294	+ 4
Dec.	0.384	55.9	3.5	0.268	322	+ 32
1888 Jan.	0.583	67.6	2.3	[0.271]	305	+ 15
Febr.	0.530	59.3	1.3	[0.307]	292	+ 2
March	0.325	50.9	3.3	0.273	289	— 1
April	0.391	59.2	6.6	0.311	320	+ 30
May	0.384	64.9	10.2	0.320	329	+ 39
June	0.188	60.0	13.4	0.279	295	+ 5
July	0.115	57.8	13.0	0.226	254	— 36

	Obsd D. R.	Bar.	Temp.	Redd D. R. I	Redd D. R. II	O. - C.
1888 Aug.	+ ^s 0.188	763.6	+ 13.1	+ ^s 0.221	+ ^s 0.263	— 27
Sept.	0.257	66.2	11.9	0.221	275	— 15
Oct.	0.304	62.6	8.2	0.220	281	— 9
Nov.	0.333	59.4	5.9	0.231	292	+ 2
Dec.	0.415	63.0	4.7	0.231	285	— 5
1889 Jan.	0.544	66.5	2.6	0.255	297	+ 7
Febr.	0.420	57.3	3.1	[0.273]	296	+ 6
March	0.437	60.6	4.4	0.279	295	+ 5
April	0.270	56.0	7.6	0.262	271	— 19
May	0.204	59.7	13.0	0.289	298	+ 8
June	0.216	64.1	15.0	0.292	308	+ 18
July	0.150	60.3	14.0	0.252	280	— 10
Aug.	0.133	59.3	13.6	0.239	281	— 9
Sept.	0.232	63.1	12.2	0.247	301	+ 11
Oct.	0.181	55.7	8.8	0.210	271	— 19
Nov.	0.408	66.9	6.4	0.215	276	— 14
Dec.	0.518	66.1	2.9	0.242	296	+ 6
1890 Jan.	0.420	60.9	4.3	0.254	296	+ 6
Febr.	0.589	67.4	2.6	0.287	315	+ 25
March	0.324	57.1	6.1	0.260	276	— 14
April	0.282	55.5	7.2	0.270	279	— 10
May	0.226	58.4	11.4	0.285	294	+ 5
June	0.282	63.6	12.4	0.295	311	+ 23
July	0.199	60.0	13.7	0.299	327	+ 40
Aug.	0.180	61.3	13.5	0.256	298	+ 13
Sept.	0.264	66.8	13.1	0.251	305	+ 22
Oct.	0.283	63.4	9.6	0.225	286	+ 5
Nov.	0.245	57.8	+ 7.1	0.198	259	— 19
Dec.	0.677	63.3	— 0.8	[0.340]		
1891 Jan.	0.711	64.8	— 0.2	[0.368]		
Febr.	0.620	73.2	+ 3.3	0.256	284	+ 15
March	0.320	56.8	4.7	0.223	239	— 28

	Obsd D. R.	Bar.	Temp.	Redd ^d D. R. I	Redd ^d D. R. II	O.—C.
1891 April	+ 0.360 ^s	760.8	+ 5.8	+ 0.236 ^s	+ 0.245 ^s	— 20
May	0.183	57.0	9.6	0.215	224	— 40
June	0.184	63.1	13.1	0.223	239	— 24
July	0.158	62.2	14.3	0.242	270	+ 7
Aug.	0.111	58.0	13.3	0.227	269	+ 7
Sept.	0.125	63.7	13.4	0.164	218	— 44
Oct.	0.136	57.4	10.9	0.198	259	— 3
Nov.	0.356	61.3	5.6	0.220	281	+ 19
Dec.	0.424	62.2	4.2	[0.238]	262	0
1892 Jan.	0.382	57.3	2.6	[0.221]	237	— 25
Febr.	0.326	56.6	3.6	0.202	230	— 32
March	0.466	63.0	3.3	[0.244]	255	— 7
April	0.375	61.3	7.3	0.285	294	+ 32
May	0.296	62.4	9.9	0.261	266	+ 4
June	0.220	62.8	12.7	0.253	254	— 8
July	0.172	63.6	13.7	0.221	231	— 31
Aug.	0.153	62.6	14.6	0.239	259	— 3
Sept.	0.169	62.7	13.0	0.212	250	— 12
Oct.	0.148	55.3	9.2	0.192	251	— 11
Nov.	0.263	62.3	7.7	0.169	234	— 28
Dec.	0.382	61.5	4.2	[0.206]	259	— 3
1893 Jan.	0.568	63.1	0.6	[0.272]		
Febr.	0.313	56.2	4.3	0.214	258	— 4
March	0.391	64.7	6.1	0.221	247	— 15
April	0.428	67.1	9.2	0.307	314	+ 52
May	0.275	64.2	11.7	0.263	261	— 1
June	0.250	63.7	13.5	0.292	290	+ 28
July	0.153	60.7	14.9	0.274	279	+ 17
Aug.	0.168	64.9	15.5	0.248	265	+ 3
Sept.	0.184	59.5	12.6	0.260	300	+ 38
Oct.	0.213	60.1	10.6	0.227	281	+ 19
Nov.	0.333	60.9	5.7	0.204	276	+ 14

	Obsd ^d D. R.	Bar.	Temp.	Redd ^d D. R. I	Redd ^d D. R. II	O.—C.
1893 Dec.	+ 0.390 ^s	762.2	+ 5.0	+ 0.224 ^s	+ 0.292 ^s	+ 30
1894 Jan.	0.459	61.3	2.5	[0.239]	278	+ 16
Febr.	0.431	62.1	4.2	[0.247]	274	+ 12
March	0.348	61.7	6.2	0.223	248	— 14
April	0.263	60.5	9.9	0.253	258	— 4
May	0.293	60.2	10.5	0.302	296	+ 34
June	0.252	62.6	12.0	0.269	258	— 4
July	0.139	60.9	15.0	0.260	237	— 25
Aug.	0.136	61.2	13.8	0.220	221	— 41
Sept.	0.246	64.7	11.9	0.232	260	— 2
Oct.	0.221	60.9	9.3	0.190	246	— 16
Nov.	0.297	63.4	7.5	0.182	253	— 9
Dec.	0.310	60.0	4.7	0.168	254	— 7
1895 Jan.	0.320	54.3	1.8	[0.181]	268	+ 8
Febr.	0.562	61.3	0.0	[0.275]	227	— 32
March	0.247	56.2	4.6	0.156	205	— 53
April	0.250	60.8	8.6	0.201	211	— 45
May	0.296	64.0	11.1	0.270	260	+ 6
June	0.273	64.6	13.6	0.306	282	+ 31
July	0.141	60.2	14.6	0.261	241	— 8
Aug.	0.133	61.1	14.6	0.241	235	— 11
Sept.	0.238	67.4	14.2	0.248	257	+ 14
Oct.	0.190	58.4	9.7	0.203	256	+ 16
Nov.	0.291	61.1	6.9	0.191	267	+ 29
Dec.	0.273	55.3	4.2	0.183	273	+ 38
1896 Jan.	0.458	68.9	3.3	0.155	241	+ 9
Febr.	0.481	72.4	4.2	0.152	216	— 14
March	0.279	58.5	5.9	0.190	229	+ 2
April	0.359	64.3	7.6	0.234	252	+ 28
May	0.356	66.2	10.0	0.269	267	+ 46
June	0.171	62.7	14.2	0.248	219	+ 1
July	0.166	64.1	14.9	0.239	217	+ 2

	Obs ^d D. R.	Bar.	Temp.	Red ^d D. R. I	Red ^d D. R. II	O.—C.
1896 Aug.	+ 0.156 ^s	762.7	+ 14.0	+ 0.226 ^s	+ 0.225 ^s	+ 12
Sept.	0.089	57.8	13.2	0.206	224	+ 14
Oct.	0.148	57.2	9.5	0.173	228	+ 21
Nov.	0.289	62.1	5.7	0.145	230	+ 25
Dec.	0.248	58.8	3.1	0.081	180	— 23
1897 Jan.	0.300	58.4	2.1	0.111	206	+ 04
Febr.	0.312	63.3	4.5	0.119	188	— 14
March	0.161	55.2	6.4	0.130	184	— 17
April	0.224	60.7	8.1	0.163	203	+ 2
May	0.191	61.4	10.9	0.195	212	+ 11
June	0.170	63.8	13.8	0.218	212	+ 11
July	0.129	63.6	14.8	0.206	192	— 9
Aug.	0.034	59.1	14.7	0.172	158	— 43
Sept.	0.174	64.1	12.0	0.170	178	— 23
Oct.	0.329	67.5	9.2	0.203	234	+ 33
Nov.	0.388	66.6	6.1	0.191	247	+ 46
Dec.	0.340	62.3	4.1	0.148	220	+ 19
1898 Jan.	0.367	70.0	5.5	0.106	167	— 34
Febr.	0.216	58.1	4.9	0.106	172	— 29
March	0.248	58.6	5.0	0.133	198	— 3
April	0.221	60.5	8.8	0.182	216	+ 15
May	0.185	58.3	10.1	0.211	235	+ 34
June	0.174	63.5	13.1	0.207	206	+ 5
July	0.181	64.8	13.4	0.205	202	+ 1

The table shows clearly that during the first months following the starting of the clock the rate has been varying rather considerably, as probably will be the case with all clocks. It will be seen at the same time that only after about 10 years the greatest regularity was attained. In the last years however the rate again began to get slightly less regular, which is shown especially in the mean rates during short periods, and when the clock was taken to pieces in 1898 it appeared that this ought not to have been deferred so long. It was

found that the pivots were more or less affected, and on the suspension-spring there was a small stain of rust, which had fortunately not eaten into the metal.

Further rather large deviations are shown by the reduced rates, whenever the temperature was below 0° . This is clearly shown by the monthly means for 1890 December and 1891 January, during which months the temperature was almost constantly below zero. It might be thought that this points to the existence of a term depending on the square of the deviation of the temperature from its mean value. Such a term might be explained by an influence of the temperature on the elasticity of the suspension-spring.¹⁾

It appeared however, as will more amply be shown below, that the monthly means show little evidence of the influence of a quadratic term, so long as the temperature remains above zero. It would seem that the temperature-coefficient changes more or less abruptly near 0° , its value for lower temperatures being much larger.

I have therefore excluded all periods during which the temperature was below 0° (or rather below -0.6° R.) Four months, *viz*: 1879 Dec., '90 Dec., 91 Jan. and 93 Jan. must consequently be excluded entirely. In 16 other months the temperature was below zero on 104 days. For these months new means were formed, excluding those days.²⁾ The following table gives the altered reduced mean daily rates, together with the corresponding mean temperatures.

	Temp.	Redd ^d D. R. I		Temp.	Redd ^d D. R. I
1880 January .	+ 2.1	+ 0.133 ^s	1891 December	+ 5.4	+ 0.208 ^s
1881 January .	+ 2.3	.199	1892 January .	+ 3.1	.195
1885 January .	+ 2.5	.161	» March .	+ 3.9	.239
1886 December	+ 4.2	.161	» December	+ 4.6	.190
1887 January .	+ 1.5	.205	1894 January .	+ 3.2	.216
1888 January .	+ 2.9	.263	» February	+ 4.9	.232
» February	+ 2.7	.264	1895 January .	+ 2.3	.174
1889 February	+ 3.4	.268	» February	+ 2.2	.146

¹⁾ Investigations by Dr. P. J. KAISER about the clock Hohwü 27, belonging to the Bureau of Verification of the Nautical instruments belonging to the Dutch navy, have shown that the nature of the suspension-spring has a considerable influence on the value of the temperature-coefficient.

²⁾ Since there were not always time-determinations exactly at the beginning and the end of each cold period, some more days had to be excluded.

These means have further been used instead of the original values.

5. The reduced daily rates I, as given in the tables above, formed the basis of the further investigation. The first 5 months have been excluded from the beginning.

To begin with, it is possible without much computation, simply by combining the reduced rates into groups, to show that they must still contain a term of yearly period which cannot be explained by a *direct* influence of the temperature.

This is done as follows. The monthly means of the rates and of the temperatures were arranged in groups of one year each, the year beginning with May and ending with the following April. Then the means were taken of the rates for each year, and the differences between the monthly means and their yearly mean were formed. Thus I derived for each year a series of 12 differences: monthly means of rate — yearly mean, and also a series of 12 corresponding temperatures. In each of these series the mean was then taken of the first and the last value, of the second and the last but one, and so on. Finally also similar results were derived substituting for the temperatures the differences between the actual temperature of the month and that of the preceding month (Δ Temp).

Then the same process was repeated with the only difference that the yearly groups commenced with February and ended with January.

The aim of this process will become clear when the results are considered. For brevity's sake I confine myself here to the five years 1884 to 1888. The differences: monthly means of rate — yearly mean are given separately for each year, and also for the mean of the five years. For the temperatures and the Δ Temp. only the means are given. The differences of the rates are expressed in thousandth parts of a second as unit.

It is evident at first sight that in the first arrangement all the series of rates show a very marked progression, while the temperatures are nearly the same. In the second arrangement the reverse is true. On the other hand the variation of the rate is roughly parallel to that of the Δ Temp. Hence the rates contain a term which does not depend on the actual temperature, but of which the maxima coincide with those of the yearly *change* of temperature, or, in other words, the yearly periodicity in the rate of the clock does not coincide with that of the temperature, and from the values just quoted we easily derive that the first lags about half a month behind the latter.

6. Before a closer investigation of the phenomenon is possible, it

	1884	1885	1886	1887	1888	84-88	Temp. 84-88	Δ Temp. 84-88
May, April.....	+39	+18	+60	+14	+42	+35	+ 8.9	+ 3 0
June, March.....	+22	+38	+32	+ 6	+27	+25	+ 8.5	+ 2.0
July, February....	+14	+28	+30	+11	- 5	+16	+ 8.8	+ 1 3
August, January ...	+11	+ 8	- 8	+ 8	-16	+ 1	+ 8.2	- 1.3
September, December	-26	-22	-40	-14	-26	-26	+ 8.5	- 1.5
October, November..	-60	-70	-77	-24	-24	-51	+ 7.4	- 3.5
February, January .	-18	+27	+ 9	+10	+ 3	+ 6	+ 3.0	- 0.8
March, December...	- 11	+27	+ 6	+ 4	- 2	+ 5	+ 4.5	- 0.2
April, November...	+ 2	+10	- 9	+ 2	+20	+ 5	+ 6.6	- 0.2
May, October	-10	-60	-10	-20	+16	-17	+ 9 6	- 0.4
June, September ...	+ 4	-14	+ 3	-15	- 4	- 5	+12.8	+ 0.6
July, August.....	+34	+ 9	+ 2	+19	-30	+ 7	+14.2	+ 0.6

must first be ascertained whether the adopted temperature-coefficient represents the observations for the whole period.¹⁾

For this purpose each year was treated separately. The years beginning with February were used, since in that case the temperature-coefficient is found nearly independent of the changes in the rate which are proportional to the time.

Gradual variations with the time are namely clearly marked, and over long periods they are not even proportional to the time. This is seen from the following summary of the yearly means in which I have taken the years beginning with May in order to be able to include 1878.

1878	+ 0.122 ^s	1883	+ 0.141 ^s	1888	+ 0.252 ^s	1893	+ 0.243 ^s
1879	.120	1884	.159	1889	.254	1894	.208
1880	.189	1885	.189	1890	.247	1895	.220
1881	.186	1886	.210	1891	.218	1896	.176
1882	.157	1887	.257	1892	.222	1897	.169

¹⁾ In the investigation of this section and also in that of § 7, it was inadvertently omitted to apply corrections amounting to 0.005 to six rates of the years '88 and '89. The influence of this omission is negligible. For the four months, in which the rates were rejected on account of the low temperatures, interpolated values were used.

Two methods have been applied to derive the temperature-coefficients. In the first method I used the deviations of the monthly means from the yearly means, while in the second the deviations of these same monthly means from approximate values of the term α , i.e. the non-periodic part of the rate, were used. These values were derived from a curve which represents as nearly as possible the yearly means for years beginning with May, with August, with November and with February ¹⁾.

These two methods gave the following series of corrections, headed I and II respectively, which must be applied to the value -0.0268 of the temperature-coefficient. They are expressed in units of one tenthousandth part of a second.

	I	II		I	II
1879	+ 15	+ 23	1889	+ 9	+ 12
1880	+ 8	+ 19	1890	+ 32	+ 21
1881	+ 47	+ 41	1891	- 11	- 5
1882	+ 70	+ 68	1892	+ 25	+ 28
1883	+ 48	+ 47	1893	+ 52	+ 46
1884	+ 29	+ 31	1894	+ 65	+ 64
1885	- 25	- 17	1895	+ 98	+ 96
1886	- 2	- 3	1896	+ 102	+ 96
1887	- 2	- 5	1897	+ 64	+ 67
1888	- 12	- 11			

The two methods thus give practically the same results. Although this agreement is of course not a measure of the real accuracy of the corrections found, it is nevertheless evident that the temperature-coefficient has not been constant during the whole period, but that the adopted value requires a positive correction as well in the first as in the last years, the latter being the most marked.

If the whole period is divided into three parts, we get the following mean results, according to the second computation (those of the first method are nearly the same):

$$\begin{array}{rcl}
 1879-1884 & \Delta c = & + 38 \\
 1885-1892 & & + 2 \\
 1893-1897 & & + 74
 \end{array}$$

¹⁾ In first approximation it was assumed that e.g. the mean for the year from '78 May to '79 April gave the value of α for '78 Nov. 1. Afterwards these values were in some cases slightly altered.

Throughout the preceding investigation it was assumed that the influence of the temperature is proportional to its first power. It is important to investigate the results which will be found, if we represent the influence of the temperature by the formula:

$$c_1(t-t_0) + c_2(t-t_0)^2.$$

For this purpose I used the deviations of the monthly means from the values of a derived from the curve. These deviations were represented by the formula

$$\Delta a + \Delta c_1(t-t_0) + c_2(t-t_0)^2.$$

I did not investigate the separate years, but I derived mean results for the three periods mentioned above; t_0 is then in each case the mean temperature of the period, and differs but little from $+8.7$ ($= +8.1$ Réaumur).

In this way I found the following values of Δc_1 and c_2 , both expressed in tenthousandth parts of a second:

	Δc_1	c_2
1879—1884	+ 30	+ 3.9
1885—1892	— 5	+ 3.9
1893—1897	+ 75	— 7.9

The values of Δc_1 nearly agree with those previously found for Δc . Those of c_2 are small and of different sign, and their reality is doubtful. The rates for temperatures below zero would require positive and much larger values of c_2 . In order to represent e. g. the two results for the months 1890 Dec. and 1891 Jan. it would be necessary to assume $c_2 = +15$.

I think therefore to have acted correctly by excluding the rates corresponding to temperatures below 0° . For the other temperatures we may certainly provisionally adopt a linear formula for the influence of the temperature.

As to the coefficient c of this formula, I do not think that it could be represented as a function of the time which would have any real meaning. Probably, however, it will be better to assume it constant during shorter periods only, e. g. thus:

	Δc	c
1879—80	+ 21	— 247
1881—83	+ 52	— 216
1884	+ 31	— 237
1885—91	— 1	— 269
1892—93	+ 37	— 231
1894—97	+ 81	— 187

Finally I will show how these coefficients would be altered (see

before) if the barometer-readings had been reduced to one temperature, in other words, what are the values of the *true temperature-coefficients*. For 760 m.m. the reduction for 1° RÉAUMUR amounts to 0,152 m.m., of which the effect on the rate is 0^s.0021. Consequently the *true temperature-coefficient* is found by applying a correction of + 0^s.0021 to the *apparent* value.

7. We shall now apply to the reduced mean rates the reductions due to the corrections found for the temperature-coefficient. The adopted corrections are of this coefficient:

1878 May—1884 April	$\Delta c = + 39$
1884 May—1893 April	0
1893 May—1898 July	+ 75

Though probably the values mentioned at the end of § 6 are preferable, it did not seem necessary to repeat the computations with these altered values.

After this the deviations of the corrected monthly means from the values of a ¹⁾ derived from the curve were formed and these means were arranged in yearly groups, each year beginning with May.²⁾ For brevity's sake I do not give the results for the separate years, but only the means for four groups of years, viz: 1879—1882, 1883—1886, 1887—1891 and 1892—1896. If the deviations of the monthly means from the yearly means are used, the mean results for those four groups are not appreciably altered. All values are given in units of one thousandth part of a second.

It will be seen that the results of the first and the second groups agree very well inter se, and also those of the third and the fourth groups, I have therefore finally formed the means for the periods 1879—1886 and 1887—1896. The principal difference between these two periods seems to be that the low minimum in October which is shown in the first, has disappeared in the last. In the years, 1892—1896, however, the whole periodicity begins to be less marked, and in 1897 it is no longer shown by the monthly means. The monthly means of 1878 (i. e. '78 May—'79 April) are in good agreement with the results for the period 1879—1886.

1) Since this curve is relative to the temperature + 10°, while the mean yearly temperature is + 8°.7 its first and last part had to be slightly altered, to account for the altered values of the temperature-coefficient.

2) The curve for a can only be drawn from '78 Nov. to '98 Jan., therefore the present investigation can only include the period '79 May—'97 April.

	79—82	83—86	87—91	92—96	1879 — 1886	1887 — 1896
May.....	+ 37	+ 38	+ 22	+ 40	+ 38	+ 31
June	+ 14	+ 24	+ 23	+ 27	+ 19	+ 25
July.....	+ 12	+ 22	+ 13	— 4	+ 17	+ 5
August ...	— 3	+ 7	— 4	— 16	+ 2	— 10
September.	— 38	— 32	— 27	— 9	— 35	— 18
October...	— 64	— 85	— 29	— 23	— 74	— 26
November.	— 22	— 54	— 26	— 21	— 38	— 24
December.	— 22	— 26	— 13	— 16	— 24	— 14
January ..	+ 12	— 5	— 7	— 6	+ 4	— 6
February .	— 1	+ 19	+ 11	— 9	+ 9	+ 1
March	+ 40	+ 34	+ 11	— 8	+ 37	+ 1
April	+ 39	+ 46	+ 30	+ 24	+ 42	+ 27

During the period 1887—1896 the periodicity can be very satisfactorily represented by a simple sinusoide. We find:

$$\Delta r = + 254 \cos 2\pi \frac{T - \text{May } 5}{365}$$

where the amplitude has been expressed in tenthousandth parts of a second ¹⁾.

For the first period such a representation is impossible, and even when a term containing the double angle is introduced, the representation is not entirely sufficient. In that case we find:

$$\Delta r = + 455 \cos 2\pi \frac{T - \text{Apr. } 24}{365} - 95 \cos 4\pi \frac{T - \text{Apr. } 23}{365}.$$

An entirely satisfactory representation can only be obtained by an empirical curve.

This curve, together with the points which indicate the observations to be represented, is here reproduced in fig. 1. The sinusoide of the second period is given in fig. 2 ²⁾.

Moreover the following table gives for the first period the differences

¹⁾ From the period 1887—1891 alone we find

$$\Delta r = + 274 \cos 2\pi \frac{T - \text{May } 1}{365}.$$

²⁾ These figures will be published together with the second part of this paper.

Obs.—Comp I and Obs.—Comp. II, where Computation I means the representation by the formula, while Comp. II refers to the curve. For the second period the differences Obs.—Comp. are also given. Everything is expressed in thousandths of a second.

	79 — 86		87—96		79 — 86		87—96
	O.—C. I	O.—C. II	O.—C.		O.—C. I	O.—C. II	O.—C.
May	+ 2	+ 2	+ 6	November .	+ 12	+ 7	+ 4
June	— 12	— 9	+ 5	December..	+ 3	— 5	+ 6
July.....	0	+ 3	— 4	January ...	+ 3	+ 1	+ 3
August.....	+ 11	+ 9	— 6	February ..	— 14	— 11	— 3
September..	+ 2	+ 3	— 2	March.....	+ 4	+ 4	— 15
October.....	— 20	— 6	— 2	April	+ 6	+ 4	+ 3

Finally attention must be drawn to the fact that a term with the argument $4\pi T$ might be explained by the direct influence of the temperature, if a quadratic term is assumed therein. In fact the yearly variation of temperature can be approximately represented by:

$$t-t_m = + 5.5 \sin 2\pi \frac{T-May 1}{365}$$

which would introduce into the rate a term:

$$\Delta r = - 15 c_2 \cos 4\pi \frac{T-May 1}{365}$$

which agrees nearly with the second term in the above formula for the period 1879—1886, if we take $c_2 = + 6$. The probability of this explanation is however lessened by the fact that a similar term does not exist after 1886.

8, The results which have so far been derived have finally been used to free the monthly means from all periodic terms and then to represent them by a simple curve.

For this purpose

1st the reduced rates I were reduced to the mean temperature $+ 8^\circ.7$.

2nd the corrections, which become necessary if the temperature-coefficients given at the end of § 6 are adopted, were applied.

3rd corrections were applied for the supplementary periodic term in the following way, viz. for 1878 to 1886 according to the curve for 1887 to 1896 by the formula, while for 1897 and 1898 the correction was adopted $= 0$.

The reduced rates found in this manner are contained in the general table of the rates given above, under the heading „Red^d D. R. II”.

The drawing of a curve was *to a large extent* arbitrary. I have tried to make it as simple as possible. It is reproduced in Fig. 3¹⁾. The residuals O.—C. (Obs. — Curve) are given in the last column of the general table.

For the years 1879—1896 the mean error of a monthly mean derived from these residuals is

$$M. E. = \pm 0^s.0237$$

If the supplementary term had not been applied it would have been

$$M. E. = \pm 0^s.0364$$

The difference is considerable.

¹⁾ The curves derived from the yearly means, which were previously used, agree with this one in the principal points, but were more complicate.

KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN
TE AMSTERDAM.

PROCEEDINGS OF THE MEETING
of Saturday June 28, 1902.

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The following papers were read:

Geology. — "*The Geological Structure of the Hondsrug in Drenthe and the Origin of that Ridge.*" By Prof. EUG. DUBOIS. (Communicated by Prof. K. MARTIN.)

(Communicated in the meeting of May 31, 1902).

North-west of Eksloo, on the Hondsrug in Drenthe, remarkable sections of the soil are now to be seen in about fifty pits, dug last winter on behalf of the projected *Noord-Ooster Lokaal-Spoorweg*.

The greatest part of these pits are found on the Noorder Veld of Eksloo, at a distance of about $1\frac{1}{2}$ K.M. from this village and at a mutual distance of 50 M., a few at 100 M. mutual distance, in the directions from north-east to south-west and north-west to south-east; some, nearer to the village, on the Hooze Veld. Seven others are on the Buiner Veld, at about $1\frac{1}{2}$ K.M. farther N.N.W. from the principal group, succeeding each other at intervals of 100 M. in the direction from south-east to north-west. The pits are square, the edges measuring about 3 M., and though many are not quite as deep now as they have been, owing to their being partly filled again by blown-in sand, the vertical sides of the greater number are still uncovered to a depth of 3 or even $3\frac{1}{2}$ M.

Excepted two of them, situated most to the north-eastern border of the Hondsrug, we observe in all a similar section. In the upper part a relatively thin bed of sand, being near the surface of a dark greyish or nearly black colour, owing to much humus contained in it, but for the rest of a light yellowish or brownish grey, this bed showing hardly any traces of stratification and containing irregularly scattered stones of very different size, among which granites and coloured quartzites are predominant¹⁾. The sand is intimately mixed in some places with a noticeable quantity of brown clay. It is the well-known *boulder-sand* of the Hondsrug. Under it, to the bottom of the pits, rather coarse, loose, white quartz-sand, which is clearly stratified and in which are to be seen, locally, irregular small banks and strings of well rounded, water-worn pebbles, principally of white vein-quartz and next to it of light-grey quartzites and Lydian Stone, the largest of which pebbles have for the greater part only a dimension of 15, some however of 25 mM. The grains of this sand seen through the magnifying-glass prove to be also well rounded and almost all clear as glass. This description of the underground is completely applicable to the "*Preglacial or Rhine-Diluvium*".

Whilst near the bottom of the pits the stratification of this pleistocene alluvium of the Rhine is often nearly undisturbed and pretty well horizontal or sloping in undetermined directions, it is upwards always fantastically folded and wrinkled, contorted, a feature becoming very prominent on account of thin or sometimes thicker veins of sand of a yellow or brown colour, evidently derived from the

¹⁾ In most cases we find only smaller stones, the bigger ones having already been dug up, which appears from the unevenness of the surface, caused by the irregular reposition of the swards. There where this is not the case, large stones and boulders are still to be found.

upper bed, alternating with the white head mass. In short, the consequences of the pressure and the moving of the land-ice with its bottom-moraine material over the loose underground are beautifully illustrated here.

Of the most part of the pits on the Noorder Veld of Eksloo, viz. of those numbered from VII to XLV, I have measured the thickness of the boulder-sand bed. These dimensions are given (in Meters) in the following small table. Some pits could not be measured on account of the indistinctness of the lower limit of the bed. From those on the Hooge Veld the thickness of the boulder-sand is not more than NW.

		XLV	XLIV	XLIII	
		0.8—1.0	0.9—1.0	0.35—0.6	
	XLII	XLI	XL	XXXIX	XXXVIII
	0.8—1.0	0.8—1.0	0.6—0.9	0.7—1.25	0.4
	XXXIII	XXXIV	XXXV	XXXVI	XXXVII
	0.7—0.8	0.6—0.7	0.6—0.8	—	0.4—0.5
	XXXII	XXXI	XXX	XXIX	XXVIII
	—	0.6—0.7	0.6—0.7	—	0.4—0.5
	XXIII	XXIV	XXV	XXVI	XXVII
	0.7—0.8	0.6—0.8	0.4—0.9	—	±0.3
	XXII	XXI	XX	XIX	XVIII
	0.7	0.3—0.5	±0.4	±0.3	±0.25
					0.8 ±1.0 cl
	XII	XIII	XIV	XV	XVI
	0.6—0.7	0.3	0.3—0.5	0.3—0.5	0.3
	XI	X	IX	VIII	VII
SE.	0.3	0.5—0.6	0.7—0.9	0.3	0.3

about 0,25 M. On the Buiner Veld (XLVIII to LIV) it varies from 0.2 to 0.8 M., attaining in a single case, locally, 1.5 M. At a distance of 200 M. north-west of XLIII there is on the Noorder Veld, near the Tippen, a pit numbered XLVI, with 0.4 M. of boulder-sand, and, 100 M. N.N.W. of the latter, another pit, numbered XLVII, showing a very irregular thickness of this upper bed, it locally giving way in the stratified white Rhine-sand. Moreover the latter contains, unto a depth of 2 M., boulders of granite and other rocks of Scandinavian origin.

From this table, that refers to an area long 400 M. in the same direction as the Hondsrug extends (from north-west to south-east) and broad 250 M., at right angle on it, and from the other given data, it appears that the thickness of the boulder-sand bed is very slight, attaining seldom 1 M., further that it varies greatly at small distances (often in the selfsame pit). The fact that the difference in height of the position of these pits is much larger than those differences in thickness, proves that the upper or boulder-sand bed follows the undulations of the preglacial nucleus of the Hondsrug and is rather regularly laid down upon it.

Some details may still be mentioned. In pit XII the brownish boulder-sand, having an average thickness of 0.6 to 0.7 M., penetrates wedgelike in the white sand unto 1.25 M. beneath the surface, whilst the strata of that underground are rent asunder unto about 2 M. lower than this wedge. This brings to the mind straining forces having worked laterally to the Hondsrug, such as would have arisen from an uplifting of the sand masses now constituting the nucleus of that ridge. In pit XXXIV two boulders from 0,2 to 0.3 M. in dimension are sunk totally below the general inferior limit of the boulder-sand bed in the pit. In pit XXXIX and XLI the sand, of a darker brown colour, is partly containing enough clay, that it becomes plastic, and also by alluviating it is proven that no small quantity of clay is present there.

But besides such particularities there are to be observed phenomena of greater importance. This is the case with N°. XLVII, showing fluvio-glacial mixing of the bottom-moraine with the sand of the underground, and with the two pits N°. XLI and XVII. In pit XLI there is in the south-western side a boulder of quartzite, almost square, about measuring 0.35 M. in every dimension. It is fixed at the bottom of the boulder-sand bed, having there a thickness of 0.7 M., and depressing, pocket-like, the strata, there rather undisturbed, of the white quartz-sand, unto 0.4 M. below its inferior extremity. Its basis is a plane ascending in the direction from north-west to south-east; but this basis belongs

properly to a sheet of the boulder, about 4 c.M. thick, extorted according to a lamination plane parallel with that sloping basis, and the large upper piece has been pushed on, sliding upward $1\frac{1}{2}$ c.M. *in the direction from north-west to south-east*. The boulder with its extorted sheet are immovably fastened in the upper boulder-sand bed, which here contains rather much clay and is tolerably hard. In the opposite side there is a somewhat larger boulder of granite, polished and scratched. The contortions in the white sand of the underground are particularly fine in this pit. Apparently no boulders were extracted here, as is shown also by the appearance of the surface.

Pit XVII, which (with XLVII) is nearest to the eastern border of the Hondsrug, at a distance of about 150 M. from the first house along the Beekslanden, shows, as already has been said, a section different from those in the other pits. Above, again the common yellowish grey boulder-sand, 0.8 M. thick, in its lower half without boulders, under this, however, ± 1 M. of reddish brown, hard boulder-clay, containing much small stone fragments and some boulders.

This hard, red boulder-clay is well known in the underground of some of the Velds of Eksloo, where, locally, it occurs, at small distances from the eastern border of the Hondsrug, as far at least as Weerdinghe.

Quite identical reddish brown boulder-clay, under 0.7 to 0.9 M. of block-sand, is visible in a clay digging at the west of the Hondsrug, along the Langhiets Kamp near Odoorn. Going from there in the direction of Valthe it soon disappears from the underground, so that the boulder-sand bed is resting immediately upon the loose Rhine-sand. In a sand digging $2\frac{1}{2}$ M. deep, at a distance of about 1 K.M. N.N.E. from Valthe, the boulder-sand is 0.4 M. thick. The white sand below it contains well rounded pebbles of white quartz and also of lydite. Halfway Odoorn and the side-branch of the Oranje Kanaal the boulder clay begins at a hundred Meter westward from the road to Emmen. There, as well as nearer to the road, where the boulder-sand rests immediately on Rhine-sand, this boulder-sand is 0.7 M. thick; but already before the side-canal the boulder-clay reaches the road which remains on it as far as Emmen. Following the high road from Odoorn in north-western direction to Ees we find the boulder-clay in a clay digging, a little farther than the churchyard, under 1 M. boulder-sand. In a well sunk still somewhat farther off, in a meadow to the right of the road, about 3 M. of this boulder-clay was met with, which contained, next to other rock species, especially flint nodules; under the clay again coarse white loose sand with small well rounded pebbles of white quartz. At a distance

of 4 K.M. from Odoorn, where the way from Eksloo to Brammershoop crosses the high road, boulder-clay is seen again, under 0.7 M. of boulder-sand; here it is partially of a yellowish brown spotted with greenish grey colour, a difference in connection with the not flowing off of the water in the soil. In sinking a well, this clay proved to have a thickness of $2\frac{1}{2}$ M. Farther north it is found at least as far as Ees.

At $2\frac{1}{2}$ K.M. south-west of Odoorn, in the Peat-moss of Odoorn, that is in the midst of the Peat-moss of Schoonoord according to LORÉ, the boulder-clay is wanting under the \pm 1 M. thick bed of boulder-sand, which came to light after the opening of the peat-moss for digging fuel. In its place a bed of light bluish grey clay, 0.3 to 0.4 M. thick, is found. This was observed at a pit dug on purpose and is the case with the whole Peat-moss of Odoorn, as has been observed when digging ditches. This plastic clay, containing no palpable sand, is entirely different from the boulder-clay. It is hardly to be doubted that we have to regard it as lake-clay, the same as the wellknown preglacial Pot-clay from the underground of Drenthe, Groningen and Friesland, which gave rise to peat-mosses in such cases where it was shaped in the form of basins.

Thus the considered part of the Hondsrug, about the half of the Hondsrug in Drenthe and almost a third of the whole of that ridge which is extended from north-west to south-east, between Groningen and Emmen, and is elevated only on an average 5 M. above the surrounding region, is constituted by preglacial Rhine-sand, superficially covered, in the same manner as the adjoining ground, by a bed of boulder-sand not 1 M. thick.

That the boulder-sand cannot owe its origin to washing out of the boulder-clay may be admitted for the following reasons:

1st The hard boulder-clay offers great resistance to eroding agencies. This appears amongst others from its forming steep and more or less projecting parts at the coast of the Roode Klif, the Mirdummer Klif and the Voorst, and even isles, at Urk and Wieringen.

2nd Though undoubtedly the quantity of boulders in the boulder-sand has from the beginning been very variable, it is however a fact, that in the neighbourhood of the villages most boulders have already been dug out and that they were formerly very numerous almost everywhere. At some places one stone was lying next to the other in the sand. An average condition is to be met with at some parts of the Noorder Veld of Eksloo. Now to the north of pit XLV on a surface of 1500 M². and to a depth of 0.5 M. there had been freshly dug out 40 M³. of stones, from the size of a child's fist up to

1 M. in length. Estimating the air spaces between the stones heaped up at $\frac{1}{4}$, we find about $\frac{1}{25}$ of the volume of the boulder-sand bed to have consisted in stones. Between pit XV and XVI a similar estimate, from a surface of 484 M²., leads to $\frac{1}{24}$ for that proportion. What an enormous thickness of boulder-clay, which in this region is particularly poor in stones, must have been washed out to leave all these stones!

3rd The boulder-sand contains very little flint, the boulder-clay very much, everywhere. Flint is the kind of rock most frequently occurring in the clay (Odoorn, Zwinderen, Nieuw-Amsterdam, Mirdummer-Klif, Nicolaasga, Steenwijkerwold, Wieringen etc.).

4th Even the deepest and evidently *not* washed out parts of the boulder-sand, which rest immediately on the Rhine-sand, are as a rule poor in clay.

5th Boulder-clay and boulder-sand are found jointly or the latter alone without this being expressed in the form of the surface.

That the Hondsrug cannot be a terminal moraine, as has been supposed by some geologists, follows sufficiently from the description of its structure as given above.

It neither can owe its origin to an upward folding or pressing of the underground, perpendicular to the direction of the motion of the pleistocene land-ice; for how then to account for the deposition of boulder-clay parallel to the Hondsrug ridge?

The distribution of the boulder-clay in our north-eastern provinces is so, that there can hardly be any doubt that from the beginning it has been very unequal and the boulder-clay has been laid down parallel with the actual Hondsrug ridge.

Can it perhaps by its weight have pressed upward the Rhine-sand, when the soil was still totally drenched with melting-water? This apparently has not been possible. The specific weight of a well compressed sample of that Rhine-sand from the Hondsrug, quite drenched with water, is 2.05. If now that of the boulder-clay had even attained the high value of 2.5, it would require a bed of boulder-clay of a thickness of 20 M. to cause an uplifting of 5 M., as is the average height of the Hondsrug above the surrounding region. In reality the thickness is most probably only $\frac{1}{7}$ of that supposed value.

Other causes must have been in action to bring about this elevation of the Hondsrug, but causes which nevertheless were not inconsistent with the deposition of the boulder-clay parallel to that ridge. These causes may be found in what CHAMBERLIN, RUSSELL, SALISBURY, VON DRYGALSKI and already NANSSEN have taught us regarding the

structure and motion of the inland-ice in Greenland. According to the earlier ideas the bottom-moraine was pushed forward under the ice, from the centrum of dispersion of the latter; to day we know that stones, sand and mud are transported included strata-like in the inferior parts of the ice mass, by the gradually melting of which the bottom-moraine is formed. Further it is known, that the motion of the inferior strata of an inland-ice mass becomes the slighter the more these are laden with stones and mud. Evidently this load was less above the strip of land which actually constitutes the eastern, most elevated portion of the Hondsrug than at the west of this portion, where the ice in its downmost parts must have been thickly laden with clay. Above this strip we may suppose to have existed a relatively more rapid motion of the inland-ice in comparison with above the extensive western clay banks, the result of which difference would have been a lower level of the ice in the first and a higher in the latter parts. Thus, actually, in Greenland a considerable diminishing of the motion and a swelling of the ice is seen there where in its undermost strata it is strongly laden with debris of rock, and lowering of the surface where this motion is not hindered, on account of the lowest ice-strata being relatively pure. Thence considerable pressure on the underground where those clay banks are now to be found in the Hondsrug and a minimum of pressure near the eastern border; there then the loose Rhine-sand, drenched with water was as a whole mass uplifted.

The situation of the elevated ridge of preglacial sand side by side with the long and broad western strip of boulder-clay makes us also suppose that the direction in which the ice moved was not, as is still generally admitted, from north-east to south-west or from north to south, but the same as the extension of the Hondsrug, from north-west to south-east. Now with this supposition perfectly agrees the at first sight paradoxical direction of motion as derived from the shifted boulder of quartzite.

But how then can we account for the fact that the boulder-clay was laid down principally in a long and broad strip along the western part, whilst the boulder-sand above it is uniformly thick with that in the eastern part on the Hondsrug where clay is generally absent under it? This question too is not difficult to solve with our actual knowledge of the phenomena of the motion of an inland-ice mass. The material of the boulder-sand bed may have been transported as a continuous bed by higher ice-strata, at the same time as disjuncted strips and patches of clay were included in the lower ice-strata, or the sand with its boulders may have been transported

at a somewhat later time. Small variations in the direction or in the velocity of the motion of the ice can easily have divided the boulderclay in strips and patches.

Thus all the observed geological phenomena can be viewed in the light of known actual phenomena, which appears to be impossible if we start from the opinions embraced up till now on the nature of the Hondsrug.

Now that it is known that the direction of ice streams which ended in North-Germany has often been considerably modified by the form of the basin of the Baltic and also by the meeting with other ice streams, it is less surprising, that, notwithstanding the predominating or exclusive occurrence of Swedish, at least Scandinavian rock species in the bottom-moraine of our north-eastern provinces, these can nevertheless have arrived there in north-west—south-eastern direction. Suchlike factors, as supposed to have modified the direction of the North-German ice streams, may have been the cause of the deviations of an ice stream, which, coming from Sweden, first took a south-western direction over Denmark, till it arrived in the North-Sea. We do not know how far the ice which came down from southern Scotland and northern England did progress south-eastward in the North-Sea; it might be possible, at least, that as a very powerful stream it has met there with the ice stream coming from Sweden and has pushed this back south-eastward in the direction of Friesland, Groningen and Drenthe.

Very likely as a result of this motion of the ice over our north-eastern provinces the Hondsrug and some parallel less extended elevations have then arisen, in such a way as indicated above. Farther west of the Hondsrug, however, probably a real folding, under the pushing ice, of strata impermeable for water, should they consist in Potclay or in the boulder-clay itself, raised, perpendicular to that direction, a number of north-east—south-western ridges, leaving between them valleys now occupied by rivulets. Indeed an elevation by folding is more readily to be admitted for compact soils than for the loose sand which constitutes the nucleus of the Hondsrug.

Geology. — "*The Geological Structure of the Hondsrug in Drenthe and the Origin of that Ridge.*" Second communication. By Prof. EUG. DUBOIS. (Communicated by Prof. BAKHUIS ROOZEBOOM).

Further researches in that part of the Hondsrug, considered in my former communication, led to the following results.

At a short distance north-east of pit LI, the boulder-sand bed of

which, up to a depth of 1.5 M., shows an irregular mixing with brown clay, there is on the highest part of the Buiner Veld (and the Hondsrug in those parts), under 0.5 to 0.8 M. of boulder-sand, a yellowish red boulder-clay bed of 1 M. thickness. It is situated at about 1 K.M. south of Buinen and measures about two hundred Meters in every direction.

The clay found in pit XVII extends, as shewn by borings, only some 50 Meters in different directions.

Another patch of boulder-clay is found south of the Zuider Esch of Eksloo on the southern Hooge Veld, in an oak-underwood, under about 0.5 M. of boulder-sand. This patch too is of small dimension. The same is the case with another on the Zuider Veld of Eksloo.

Farther, in the neighbourhood of Valthe, a clay bed is found on the Kwabben Veld, under \pm 0.5 M. of boulder-sand, 1.5 M. thick, at least, of about 300 M. dimension in every direction and extending still somewhat farther south-east on the Nieuwe Esch; a smaller one exists south-east of the Kampen Veen.

The four latter clay patches are situated, with the two first mentioned, pretty well in one direction, from north-west to south-east, but they are separated by large intervals in which the boulder-sand rests immediately on preglacial stratified white Rhine-sand. The mutual distances of these clay patches are resp. 2, 3, 1, 2, 1.5 K.M. With the only exception of the small clay patch on the Noorder Veld, all these, though situated very near to the eastern border of the Hondsrug, are on the highest parts of that ridge.

The stratified white Rhine-sand is, amongst other localities, to be seen in a sand digging on the Kleine Esch of Eksloo (under \pm 0.4 M. of boulder-sand) in a sand digging at the northern border of that Esch (under 0.3 M. of boulder-sand) and on the Zuider Veld, near to the southern border of the Achter Esch; further at the Valther Schans (under 0.3 or 0.4 M. of boulder-sand), in a sand digging east of the Kampen Veen (under a bed of boulder-sand of the same thickness) and further, along the great Bourtaanger Peat-moss, from Valthe to Weerdinghe.

The western boulder-clay, on the contrary, forms a long and broad strip, which from Ees to Emmen seems not to be interrupted and is 1 to $1\frac{1}{2}$ K.M. wide. It has probably in its whole length a thickness of 2 or 3 M. and is covered by 0.7 to 1 M. of boulder-sand.

The origin of the Hondsrug according to the hypothesis indicated in the former communication can thus only be applied to that western strip of boulder-clay. Other facts now observed have brought to my mind, besides the already mentioned factors, others which may have

been of still greater importance in the formation of the Hondsrug.

Beyond the Hondsrug also, even as far west as Hoogeveen, the underground consists of preglacial "Rhine-Diluvium". In the Peat-moss of Ees it is covered by at most 1 M. of boulder-sand. In the Elders Veld between Schoonoord and Schoonloo the preglacial Rhine-sand is of a yellowish grey colour, on account of its intimate mixing with parts of the upper bed. The occurrence of small water-worn pebbles of white quartz and lydite, repeatedly stated to a depth of 2 M., serves to show, that here too we have chiefly before us old Rhine-alluvia, which only later on were mixed with the bottom-moraine. At Schoonloo, in a sand digging, a kind of "Mixed Diluvium" (*Gemengd diluvium*) is to be observed; water-worn pebbles of white quartz and lydite are seen in the sand side by side with Scandinavian granites. On the Elders Veld boulder-clay is only found in single small patches, such as the one at 1.5 K.M. south-west of Schoonloo.

In the midst of the Peat-moss of Ees, at a distance of 4 K.M. exactly south from Westdorp, a round hillock rises above the perfectly level environs, not unlike a small volcanic island above the sea. With a basis of about 30 M. of diameter and a height of circa 5 M. it resembles a very large tumulus; it is the renowned Brammershoop.

The constitution of this hillock, however, is inconsistent with the idea, which presents itself at first sight, that we have before us a work of mans making. It is indeed composed of white quartz-sand with well rounded small pebbles of white quartz and lydite, the same preglacial Rhine-sand, which also constitutes the underground of the surrounding region with a mantle of glacial boulder-sand only 0.2 to 0.5 M. thick.

Still less than in the case of the Hondsrug it will do here, to attribute the origin of the elevation to pressure of the pushing ice; for how could the motion have been directed from all sides towards that single point! As it appears to me, the only way to explain how only there the soil was pressed upward, in the form of an isle, is to suppose that a minimum of pressure of the ice, has existed there, most probably in consequence of a former *Gletschermühle* (*moulin*) in the period of the melting of the ice.

Not improbably then we have, partially or perhaps chiefly, to impute the elevation of the preglacial Rhine-sand in the Hondsrug to a similar minimum of ice-pressure, at the place of a large river-bed, formerly occupied by melting water, and carved in the surface of the ice in the direction from north-west to south-east, or may-be to a large and long crack in the same direction.

Zoology. — "*On the Shape of some Siliceous Spicules of Sponges*";
by Dr. G. C. J. VOSMAER.

The perplexing amount of variety exhibited by sponge spicules has since long made it desirable 1st to designate certain spicules by special terms, and 2nd to divide the spicules into groups. The first attempt to such a classification was made by BOWERBANK in 1858; later, in 1864, modified by the same author. BOWERBANK divided (1864 p. 13) the spicula into "essential skeleton spicula" and "auxiliary spicula". It is obvious that this primary classification is not based on morphological characters. Since KÖLLIKER (1864) has pointed out the morphological value of the axial canal or, more correctly, the axial thread ("Centralfaden"), OSCAR SCHMIDT has rightly based his classification of siliceous spicula on the presence of one or more of such axial threads, which after all represent the axes of the spicula. SCHMIDT distinguishes (1870 p. 2—6) four types of spicules:

1. "Die einaxigen Kieselkörper."
2. Die Kieselkörper, deren Grundform die dreikantige reguläre Pyramide."
3. Die dreiaxigen Kieselkörper."
4. Die Kieselkörper mit unendlich vielen Axen."

Neither GRAY (1873, p. 203—217), nor CARTER (1875, p. 11—15) understood the fundamental value of SCHMIDT's classification. My attempts to draw attention to it (1881 *a* and 1884 p. 146—168) have had but little influence. Thus, in 1887, RIDLEY & DENDY divide the spicula of the Monaxonids in the first place into Megasclera and Microsclera, a classification which practically agrees with those of BOWERBANK and CARTER. The example was followed by SOLLAS in spite of his being well aware of the fact that the distinction is far from "absolute". This author quite correctly remarks (1888, p. LIII): the microscleres and megascleres pass into each other by easy gradations, so that it is not possible to say where one ends and the other begins, indeed there would be a certain convenience in accepting a third division of intermediate or middle-sized spicules, which we might call mesoscleres." Finally, in 1889, SCHULZE & LENDENFELD accept SCHMIDT's primary division into "polyaxone, tetraaxone, triaxone, and monaxone Nadeln."

I do not intend to discuss here the triaxons and tetraaxons; for the present I only wish to draw attention to some monaxons and some spicules hitherto generally considered as polyaxons.

In the group of the monaxons, i. e. spicula with one single axis, two fundamental divisions may be distinguished, according to the

fact whether the ideal axis lies in a plane or not. In the former case the line may of course be straight, curved, bent, flexuous etc.; in the latter case the line is a screw helix ¹⁾. The spicula belonging to the former case I propose to call *pedinaxons* ²⁾, the others *spiraxons* ³⁾. To the group of the pedinaxons belong e. g. oxea, styles, tylostyles, some of the "amphidisci", some of the "toxa". It is, however, to the spiraxons, that I wish more especially to draw attention.

Again we can distinguish here two cases: α . the screw line is formed on the surface of a circular cylindre or β . on that of an elliptical cylinder. The former group I wish to call α -*spiraxons*; the pitch is here generally large. The latter I call β -*spiraxons*; the pitch is here small.

Let us first examine the α -spiraxons. To this group belong the spicula known as sigmaspires, toxaspire, spirules; further those which are usually called spirasters and which are by the majority of spongiologists erroneously considered as modified asters. This mistake is due, I believe, to OSCAR SCHMIDT. „Eine blosse Modification dieser Kugelsterne," he says, 1870, p. 5, „sind die Spiralsterne oder Walzensterne. Sie werden zwar in manchen Spongien nur allein, d. h. nicht untermischt mit den Kugelsternen angetroffen (*Spirastrella cunctatrix* Sdt. *Chondrilla phyllodes* N.), häufiger aber, wie wir unten in die Specialbeschreibung (z. B. von *Sphinctrella horrida* N. und *Stelletta hystrix* N.) hervorheben werden, liegen alle Uebergänge von den normal centralen Sternen zu den gezogenen Spiralsternen vor." Unfortunately did SCHMIDT not keep his promise; for in the description of *Sphinctrella horrida* we find nothing more about it, and *Stelletta hystrix* is forgotten altogether. SCHMIDT failed, therefore, to give any proof whatever for his statement that "Spiralsterne" are modified "Kugelsterne". SCHMIDT's suggestion has nevertheless generally been accepted, myself not excluded.

SOLLAS (1888, p. LXI) distinguished two chief series of spicula (microsclera): "the radiate or astral, and the curvilinear or spiral." The former are called "asters," the latter "spires." With some astonishment we further read that the asters are divided into two

1) These terms are to be taken cum grano salis. No biological formation will ever be absolutely mathematical; thus it may be that the axis of a flexuous or undulating spiculum is not exactly lying in a plane, without, however, being in any way comparable to a screw helix.

2) πεδινός, plane, even.

3) σπειζα (lat. spira), everything which is twisted.

subsections: "the true asters or euasters, and the streptaster or those in which the actines do not proceed from a centre but from a larger or shorter axis, *which is usually spiral*". Evidently one should expect that those "streptasters" were arranged under the "spires." As a matter of fact neither SOLLAS, nor any other author has given very striking arguments to consider the spiraster as a modification of the euaster. We know examples of very young stages of spirasters; they always possess the twisted character. But no instance is known of spirasters originating from or forming transitions to true asters. It is true that such supposed transitions are mentioned by some authors; but probably we have here to do with a mistake due to optical delusion. For instance, SCHMIDT described (1862, p. 45) a *Tethya bistellata*, possessing in addition to ordinary asters, double ones ("Doppelsterne"). But LENDENFELD described (1897, p. 55—58) a *Spirastrella bistellata* (which he considers identical with *Tethya bistellata* O.S.), in which he found that the supposed asters are true "spirasters". Judging from what I saw in a type specimen of SCHMIDT's sponge, I have no doubt that LENDENFELD is right. Quite correctly LENDENFELD believes that SCHMIDT has been misled by an optical delusion, "da diejenigen Spiraster deren Axen im Preparat aufrecht stehen und daher verkürzt gesehen werden, häufig wie Euaster aussehen". I fail to find a single proof that spirasters are modified euasters, either in previous papers, or in my preparations. On the contrary, everything speaks in favour of the view that "spirasters" are a sort of α -spiraxons. The fact that in some cases it is difficult to get certainty about the twisted shape, is no proof against my suggestion in general. For in the great majority of cases the twisted nature is certain, as can be demonstrated by allowing the spiculum to roll in the preparation when observed through the microscope.

Let us proceed now to examine the *different sorts* of α -spiraxons.

1. *Sigmaspira*.

SOLLAS (1888, p. LXII) gives the following definition of the sigmaspira: "a slender rod, twisted about a single revolution of a spiral"; he adds that it appears in the form of the letter C or S, according to the direction in which it is viewed. The definition of the "toxaspire" runs as follows: "a spiral rod in which the twist a little exceeds a single revolution. The pitch of the spiral is usually great and the spicule consequently appears bowshaped when viewed laterally". . . . It seems to me not quite exact when SOLLAS pretends that the bowshaped appearance is in the first place due to the number of revolutions.

Considering the facts that these spicula are generally very small, and that consequently a microscope of very high power is wanted to understand the true shape, it is evidently not easy to determine the number of entire revolutions or parts of it; the same may be said of the pitch of the "spiral" — or rather of the screw helix.

In order to obtain certainty about this I constructed wax models, the axis of which were screw helices of various length and various pitch, of course all drawn on the same circular cylinder. The diameter of the models I made in accordance to the relative size observed in the spicula. Such a set of models ought to be carefully studied *in projection*. This can be done by looking at them with one eye, or, which is far better, by studying the shadows of the models in various positions. These projections are then compared to the camera-drawings or microscopical projections of the spicula themselves. This method most clearly shows 1st that the bow-shape can be obtained with models of less than one revolution; 2nd that the C- or S-shape can be obtained with models of more than 1½ revolution. This depends both on the length and the pitch of the screw helix, as is shown by the following table ¹⁾:

Number of revolutions.	Pitch.			
	10°	20°	30°	40°
2/3	C — —	C [S] (A)	C [S] A	
3/4	C [S] —	C S (A)	C S A	
5/6	C (S) [A]		C S A	C S A
1	[C] (S) [A]	(C) S A	C S A	C S A
1 1/6	— [S] (A)	(C) S A	C S A	
1 1/4	— (S) A	(C) S A		C S A
1 1/3	— (S) A	C S A	C S A	
1 1/2	— (S) A	(C) (S) A		C (S) A
1 3/4	— [S] (A)	— [S] A	— — A	— [S] A
1 5/6			— — A	
2	— — —	— — —		— — [A]

¹⁾ C, S or A means: C-shape, S-shape or bow-shape distinct; () means indistinct; [] means very indistinct. A dash — means that the shape cannot be obtained with the wax model.

This result leads us to a dilemma. Either the definitions of sigma-spira and toxaspira will have to be modified, or we have to drop the distinction between the two forms of spicula. I believe that it follows from the above table that the latter way out of the difficulty is preferable. We may maintain the name sigmaspira for smooth, i. e. not spined α -spiraxons of no more than $1\frac{1}{2}$ revolution.

LENDENFELD (1890 p. 425) has another conception of the sigmaspira : "ein einfach spiralig gewundener oder bogenförmiger Stab." Hence he seems to accept two different kinds, instead of considering them as belonging to one sort, the shape of which simply differs according to the direction in which it is viewed. Since he says that his "spirul" has "mehr wie eine Windung", he seems to accept no more than one revolution for the sigmaspire. This is not in accordance with my observations, as laid down in the above table.

2. *Spirula*.

Although CARTER did not give a special definition of the spirula, it is clear enough what he understands by this name. In his paper on the "spinispirula" (1879 α p. 356) he calls the spiculum which he formerly (1875 p. 32) described as "sinuous subspiral", simply "the smooth form of the spirula" and he refers to an illustration of the spicule as it occurs in *Cliona abyssorum* (1874, Pl. XIV, p. 33). Obviously the term spirula used by CARTER is an abbreviation of "spinispirula", not as terminus technicus. RIDLEY & DENDY (1887 pp. XXI and 264) introduce the term spirulae as synonym with spinispirulae of CARTER, adding that "these are more or less elongated, spiral or subspiral forms, which may be either smooth or provided with more or less numerous spines." SOLLAS creates (1888 p. LXII) the term polyspire for spirula, stating that it is "a spire of two or more revolutions", adding, however, that he is inclined to adopt the term spirula. In the list given by SCHULZE & LENDENFELD (1889 p. 28) we find a "spirul" described as "spiral gewundene Nadel mit mehr als einer Windung". Consequently we learn that the term spirula by some authors is used both for smooth and for spined forms, whereas others leave the question open. LENDENFELD (1890 p. 426) proposes the name for smooth spicula only : "eine schlanke und glatte, spiralig gewundene Nadel mit mehr wie einer Windung". I herein agree with LENDENFELD and I understand by spirula : a smooth α -spiraxon of at least $1\frac{3}{4}$ revolution.

3. *Spinispira*.

As long as the α -spiraxons are smooth it will as a rule not create any difficulty to distinguish sigmaspirae and spirulae. But there are

a quantity of spined α -spiraxons. Evidently such spined α -spiraxons will exhibit the twisted nature the less distinctly the more the spines are developed. It is, therefore, not practical in this case to make distinctions, based on the number of revolutions. Especially not because there exists a great diversity with many transitions. I prefer, therefore, to propose for spined α -spiraxons the general term spinispirae, to which I bring the spicula called by previous authors spirasters, metasters, plesiasters, and also (partly) spinispirules, sanidasters etc.

SOLLAS (1888 p. LXIII) has given the following definition of the spiraster: "a spire of one or more turns, produced on the outer side into several spines." SCHULZE & LENDENFELD (1889 p. 28) say that it is a "leicht gewundener gestreckter Aster mit dickem, dornenbesetztem Schaft", a definition which LENDENFELD (1890 p. 426) modified into: "ein kurzer und meist dicker, leicht spiralig gewundener Stab mit starken, meist dicken und kurzen, kegelförmigen Dornen". SOLLAS distinguished "metasters" and "plesiasters" from his spirasters, but he acknowledges himself that: "the three forms present a perfect gradational series, so that it is frequently difficult when they all occur associated in the same sponge, to distinguish in every case one variety from the other". Now it happens very frequently indeed that they all occur associated in the same sponge and that all gradations are met with. One only needs to read SOLLAS' own descriptions and to compare them with his illustrations, e. g. of the many "species" of *Thenea*, *Poecillastra*, *Sphinctrella* i. a. in order to become convinced that it is practically impossible to distinguish spirasters, metasters and plesiasters. SCHULZE & LENDENFELD, therefore, did not adopt the latter two terms.

I am of opinion that the name spinispira can be likewise applied to the spicula which SOLLAS calls amphiaser; at any rate to such amphiasers as are said to occur in *Stryphnus niger* SOLL. ¹⁾ A great confusion exists, with regard to the word amphiaser. The name is first used by RIDLEY & DENDY (1887 pp. XXI and 264), who say that the amphiaser is composed of "a cylindrical shaft bearing a single toothed whorl at each end; occurring for example, in *Aconiderma mirabile*..." The authors give an illustration by fig. 9 on their Pl. XXI, and a further explication saying: "amphiastra = birotulates (Bowerbank); amphidisks (auctorum)." But SOLLAS says (1888 p. LXIV) of his amphiaser "the actines form a whorl at each extremity of the axis, which is straight"; herewith a woodcut on p. LXI.

¹⁾ In his preliminary account on the Challenger-Tetractinellids (1886 p. 193) SOLLAS calls this spiculum "amphiastrella".

SCHULZE & LENDENFELD (1889 p. 8) have about the same conception of the spiculum: "gestreckter Aster; ein Schaft, von dessen beiden Enden Strahlen abgehen." Comparing now the three quoted illustrations, it becomes evident that there are important differences between them. Notwithstanding SCHULZE & LENDENFELD illustrate a spicule with a long "Schaft" and long pointed "Strahlen", we find in the definition of LENDENFELD (1890, p. 419) that the amphiaser is: "ein in die Länge gezogener Stern, die aus einem *kurzen*, geraden Schaft besteht, von dessen Enden mehrere *kurze* Strahlen abgehen". Indeed: tot capita tot sensus. If, therefore, I bring certain amphiasers to the spinispirae, only such are meant as SOLLAS describes e.g. in *Strypplinus niger*.

CARTER (1879 a, p. 354—357) has introduced the term "spinispirula" for spiniferous spirally twisted spicules." Such spicula are, according to CARTER exceedingly polymorph. They may be "long and thin" or "short and thick". The spines may be "long and thin . . . or long and thick . . . or obtuse . . . The spines may be arranged on the spicule in a spiral line, corresponding with that of the shaft . . . or they may be scattered over the shaft less regularly . . . Lastly, the shaft may consist of many or be reduced to one spiral bend only . . ."

Instead of choosing one of the various terms mentioned above, I prefer the new term spinispira, which is then simply: a spined α -spiraxon. If in future it happens become to a desideratum to have more than one name for such spicula, one might distinguish two groups of spinispirae, viz. forms with long spines and such in which the spines are small, in comparison to the total length of the spiculum. In the former group the ratio between the length of the spines and the total length is usually no more than 1 : 3; very seldom as much as 1 : 7; the number of revolutions is generally not more than $1\frac{1}{2}$. In the latter group this ratio is usually at least 1 : 10; the number of revolutions as a rule more than two.

4. *Microspira*.

In some sponges very minute spicula occur, especially in the superficial (dermal) layers and lining the canals, which are either distinct α -spiraxons, or modifications by reduction. For obvious reasons it can only be made out with a microscope of very high power and in favourable situation in the preparation, whether they are smooth or minutely spined. In such small spicula it is not always possible to distinguish with certainty whether they are minute spinispirae, sigmaspirae or spirulae. Moreover they show generally manifold transitions in one and the same sponge specimen. This is e.g. the case in *Placospongia*

carinata. And still, we want to designate them with a name; I propose to use for this the term *microspira*.

5. *Sterrospira*.

In the remarkable genus *Placospongia* the stony cortex and axis are almost entirely composed of spicula, which very strikingly resemble the sterrasters of Geodidae. Keller (1891 α , p. 298) was the first to demonstrate that these spicula are of quite a different nature; whereas the sterrasters develop from true asters, the cortical spicula of *Placospongia* take their origin from "Spirastern". This observation is confirmed by LENDENFELD (1894 δ , p. 115). HANITSCH (1895, p. 214—216) found the same for the corresponding spicula of *Physcaphora* (= *Plancospongia*) *decorticans*; as they possess in this species an elongated, somewhat crescent-shaped appearance HANITSCH called them "selenasters". In 1897 LENDENFELD, not acquainted with the paper of HANITSCH, proposed the name "pseudosterrasters" for the cortical and axial spicula of *Plancospongia graeffei* (= *Physcaphora decorticans* Han.). If one wishes to apply the rules of priority in this case, the spicula under consideration have to be called selenasters. I am, however, of opinion that these rules, excellent as they are for specific nomenclature, need not to be applied in other cases and I propose, therefore, the name *sterrospira*, which at the same time reminds us of the sterrasters (of the Geodidae) and the spiraxons.¹⁾

In the group of the β -*spiraxons* the ideal axis of the spiculum is a line drawn on an elliptical cylinder. The simplest type of such a spiculum is

1. *Sigma*.

This term is introduced by RIDLEY & DENDY (1887, pp. LXIII and 264) for spicula called by BOWERBANK "bihamate", "contort bihamate" and "reversed bihamate". The authors say that the sigma consists of a "slender, cylindrical shaft, which is curved over so as to form a more or less sharp hook at each end. The two terminal hooks may curve both in the same direction, when the spicule is said to be simple... or they may curve in different directions, when it is said to be contort... There is, however, no real distinction between the two, and, as a matter of fact, the spicules are nearly always contort to some extent". SOLLAS (1888, pp. LXII) modified the definition into "a slender rod-like spicule curved in the form of the letter C. This spicule is not spiral though it probably arises

¹⁾ For details I refer to a paper on *Placospongia* from Dr. VERNHOUT and myself, to appear within a short time (Siboga-Expeditie. Monogr. VI. Porifera).

from a sigmaspire by increase in size and loss of the spiral twist". SCHULZE & LENDENFELD (1889, p. 28) stick to the contorted nature: "gewundene, eine halbe Spiralwindung bildende Nadel". Finally the definition is again somewhat modified by LENDENFELD (1890, pp. 426): "einfach spiralig gekrümmter oder bogenförmiger Stab."

The spicula belonging to this type, appear, like the sigmaspirae in the shape of the letter *C* or *S*, or as a bow. Here too these various appearances depend on the direction in which the spiculum is viewed. According to my conception only such forms belong to this group, which are contorted, not such in which *really* the "hooks curve both in the same direction". The latter are curved pedinaxons, the former are spiraxons. The axis, as a rule, has less than one, but more than half a revolution, which is easily proved by wax models.

As a derivation or modification of the sigma we have

2. *Chela*.

BOWERBANK has already shown (1858, p. 304—305; reprinted 1864 p. 47—48) that the chelae develop from sigmata. This observation is confirmed and enlarged by RIDLEY & DENDY (1887, p. XX), LEVINSSEN (1886 and 1894), H. W. WILSON (1894), PEKELHARING & VOSMAER (1898, α p. 36—38). We remarked (l. c. p. 37): "not only can we confirm this but we can give a new strong argument in favour of it. This lies in the fact that the anisochelae of *Esperella syriac* are twisted." I can add now that this twisted nature is found in isochelae as well as in anisochelae. Consequently we may regard both as β-spiraxons.

3. *Diancistra*.

According to RIDLEY & DENDY (1886, p. XIX) the spicula, which BOWERBANK called "trenchant contort bilaminate", and for which they propose the name diancistra are "usually . . . more or less contort, the two hooks lying in two different planes". My own observations confirm this statement and I bring the diancistra, therefore, likewise to the β-spiraxons.

Resuming we may divide the monaxons into the following primary groups:

- I. *Pedinaxons*. Monaxons the axis of which lies in a plane; (oxea, styles, tylostyles, etc.).
- II. *Spiraxons*. Monaxons the axis of which is a screw helix.
 - A. α-*Spiraxons*. The axis is a line drawn on a circular cylinder; the pitch is generally great, to this group belong:

1. *Sigmaspira*.; smooth α -spiraxon of no more than $1\frac{1}{2}$ revolution.
 2. *Spirula*; smooth α -spiraxon of at least $1\frac{3}{4}$ revolution.
 3. *Spinispira*; spined α -spiraxon.
 4. *Microspira*; very minute, smooth or spined α -spiraxon; it unites the characters of 1 and 3 diminiutively, and frequently forms transitions and reductions.
 5. *Sterrospira*; the young stages are spinispirae, from which develop by secondary soldering together of the spines the adult forms.
- B. β -*Spiraxons*. The axis is a line, drawn on an elliptic cylinder; the pitch is always small; always less than one revolution. Hereto belong:
1. *Sigma*; smooth β -spiraxon.
 2. *Chela*; the young stages are sigmata; in course of development very complicated siliceous processes grow out; we distinguish two sorts, viz. isochelae and anisochelae.
 3. *Diancistra*; the young stages are (probably) sigmata from which develop the adult ones by outgrowth of siliceous processes.

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Physics. "*Statistical electro-mechanics.*" II. By Dr. J. D. VAN DER WAALS Jr. (Communicated by Prof. VAN DER WAALS.)

The distribution of the energy over the different periods in quasi-canonical ensembles.

In equation (8) of my previous communication ¹⁾ a distribution of the energy over the different periods is included. If therefore this equation really represents the condition of a space filled with "black radiation", then a complete spectral formula for black radiation may be derived from it with the aid of the law of WIEN on the shifting of the wave-length with the temperature.

Instead of discussing the rather intricate equation (8) I have taken a simpler equation which I expected to yield the same distribution of the energy over the different periods. This simpler equation, however, proves to include a distribution which does not at all agree with the distribution of the energy which is found in black radiation. Now it is possible that the distribution, determined by the simpler equation does not agree with that, determined by equation (8). But it is also possible and for the present this seems more likely to me, that equation (8) does not represent the condition of a space filled with black radiation, or in other words that the nature of black radiation is not correctly determined by the suppositions that ϵ , φ and χ have a most probable value, and that for the rest the distribution is as irregular as possible. If this second explanation is the true one, the systems are still subjected to other conditions, besides those concerning the most probable values of ϵ , φ and χ , or, what comes to the same, the distribution of the systems of an ensemble in which the conditions for the values of ϵ , φ , and χ are satisfied, are moreover still partially ordered.

The simplification I have applied to equation (8) is the following. In the first place I have omitted $\frac{\omega}{\delta_2}$; this will no doubt have very

¹⁾ These Proceedings IV, p. 27.

little influence on the distribution of the energy. Then I have confined myself to treating one dimension only, and this has induced me to omit the terms $\frac{\Omega_e + \Omega_m}{\sigma_1}$. If, however, we admit electric and

magnetic masses into the space, statical forces may occur. When analysed with the aid of FOURIER'S integrals these statical forces actually yield a distribution of the energy over the different wavelengths. Yet they do not contribute to the propagation of radiation, the distribution of which we wish to investigate. It is for this reason that I have preferred a distribution in time to one in space.

So we consider the component f' in a certain point during the time between the moments $t=0$ and $t=t_1$. This time we think divided into n equal parts τ and the values of f' during those parts we call respectively $f'_1, f'_2, f'_3, \dots, f'_n$. Then the index of probability gets the following value:

$$\eta = \frac{\psi}{\vartheta} - \frac{1}{\vartheta} \int_0^{t_1} f'^2 dt - \frac{1}{k} \int_0^{t_1} \frac{df}{dt} dt \quad . \quad . \quad . \quad . \quad (8a)$$

If we wish to make the agreement of this equation with equation (8) as great as possible, we have to give to k in this equation $4\pi V^2$ times the value it has in equation (8); this follows from the equations (10) and (15).

Now we will proceed to the investigation of the distribution of the energy over the different periods, included in equation (8a). To that purpose we represent f' as a function of t during the space of time between $t=0$ and $t=t_1$, by means of the integrals of FOURIER. As we will begin with treating f' as a discontinuous function, determined by the n values f'_1, f'_2, \dots, f'_n , we will represent the integral as a sum, which only becomes an integral if we make n assume the limiting value ∞ . Therefore in the expression

$$f(t) = \iint f(u) \{ \sin(uq) \sin(qt) + \cos(uq) \cos(qt) \} du dq, \quad . \quad . \quad (26)$$

in which the limits for u are 0 and t_1 and those for q are 0 and ∞ , we will replace u by $\frac{t_0}{n} v$ or by τv and du by τ where v represents the series of the integers between 0 and n .

So we get

$$f(t) = \tau \sum_{v=0}^{v=n} \int_0^{\infty} f_v \{ \sin(\tau v q) \sin(qt) + \cos(\tau v q) \cos(qt) \} dq.$$

If we wish to separate in this equation the energy for a deter-

mined period we must give η a determined value ρ and then take the square of the amplitude for this vibration. So we find:

$$A_p = \tau^2 \left\{ \sum_{v=0}^{v=n} f_v \sin(\tau v p) \right\}^2 + \tau^2 \left\{ \sum_{v=0}^{v=n} f_v \cos(\tau v p) \right\}^2.$$

In what follows we may omit the limits as all summations are to be executed between 0 and n ; and we may omit the constant factor τ^2 as it is only our aim to determine the relative values of quantities A_p for different values of p . So we get:

$$\begin{aligned} A_p &= \sum \sum f_v f_{v'} \{ \sin(\tau v p) \sin(\tau v' p) + \cos(\tau v p) \cos(\tau v' p) \} \\ A_p &= \sum \sum f_v f_{v'} \cos(v-v') \tau p \dots \dots \dots, \quad (27) \end{aligned}$$

For this quantity A_p we seek the mean value for all systems of the ensemble. To this purpose we have to multiply the value of equation (27) with the probability that the quantities $f_1 \dots f_n$ have a determined, arbitrarily chosen value and consequently we have to integrate according to $df_1 \dots df_n$ between the limits $-\infty$ and $+\infty$.

To that purpose we will represent $\frac{df}{dt}$ by $\frac{f_{v+1} - f_v}{\tau}$, and we get:

$$A_p = \int e^{\frac{\psi - \tau \sum f_v^2}{\theta} - \frac{\sum (f_{v+1} - f_v)^2}{k\tau}} f_v f_{v'} \cos(v-v') \tau p df_1 \dots df_n \dots \quad (28)$$

If we bring the factor $e^{\frac{\psi}{\theta}}$ outside the integral sign as well the exponent of e as the other factor under the integral sign are homogeneous quadratic functions. By the introduction of other variables we may transform both functions to terms of n squares and in the same time it is possible to choose the variables in such a way, that all coefficients which occur in the exponent are unity. So we may bring the integral into the following form:

$$\int e^{-(\varphi_1^2 + \varphi_2^2 + \dots + \varphi_n^2)} (\beta_1 \varphi_1^2 + \beta_2 \varphi_2^2 + \beta_3 \varphi_3^2 \dots \beta_n \varphi_n^2) \Delta d\varphi_1 \dots d\varphi_n \quad (29)$$

where Δ represents the determinant of JACOBI. The linear substitution required to get this form may be thought to be executed in two operations: 1st a substitution which yields

$$\chi_1^2 + \chi_2^2 \dots \chi_n^2$$

for the exponent and:

$$a_{11} \chi_1^2 + a_{22} \chi_2^2 + \dots + a_{nn} \chi_n^2 + 2 a_{12} \chi_1 \chi_2 \dots + 2 a_{(n-1)n} \chi_{n-1} \chi_n$$

for the other factor; 2nd an orthogonal substitution in consequence of which both functions assume the form they have in equation (29).

The determinant of JACOBI for the total substitution is the product of the determinants for the partial distributions. The determinant

for the orthogonal substitution has the value unity; so only the determinant for the first partial substitution remains. This substitution has been chosen without taking into account the form of the second factor. The coefficients which determine this substitution depend therefore only on the coefficients of the exponent; as p does not occur in these coefficients, the determinant also cannot be a function of p , and so we may omit it in what follows.

The integral (29) can easily be integrated and yields:

$$C \sum \beta$$

So we have only to calculate the sum of the coefficients β . These coefficients may be found by the solution of the following equation of which they represent the n roots:

$$\begin{vmatrix} a_{11}-\beta & a_{12} & a_{13} & \dots & a_{1n} \\ a_{21} & a_{22}-\beta & a_{23} & \dots & a_{2n} \\ a_{31} & a_{32} & a_{33}-\beta & \dots & a_{3n} \\ \dots & \dots & \dots & \dots & \dots \\ a_{n1} & a_{n2} & a_{n3} & \dots & a_{nn}-\beta \end{vmatrix} = 0. \quad (30)$$

The sum of the coefficients β is the sum of the roots of this equation, i.e. the coefficient of β^{n-1} . Only the product of the elements of the diagonal of the determinant yields terms containing β^{n-1} ; and as is obvious, the coefficient of β^{n-1} will be

$$a_{11} + a_{22} + a_{33} + \dots + a_{nn}$$

In order to determine this sum we have to find an arbitrary substitution for which the exponent assumes the form $\sum \chi^2$ and then we must substitute the new variables χ into the second factor. A substitution fulfilling this condition may easily be found. The exponent namely may be written as follows:

$$\frac{\tau}{\vartheta} \sum f_v^2 + \frac{1}{k\tau} \sum (f_{v+1} - f_v)^2 = \sum (a f_v - \beta f_{v+1})^2$$

where:
$$a^2 + \beta^2 = \frac{\tau}{\vartheta} + \frac{2}{k\tau} \quad \text{and} \quad -2 a \beta = -\frac{2}{k\tau}.$$

So we find for a and β :

$$a = -\frac{1}{2} \sqrt{\frac{\tau}{\vartheta} + \frac{4}{k\tau}} + \frac{1}{2} \sqrt{\frac{\tau}{\vartheta} + \frac{4}{k\tau}}, \quad \beta = \frac{1}{2} \sqrt{\frac{\tau}{\vartheta} + \frac{4}{k\tau}} - \frac{1}{2} \sqrt{\frac{\tau}{\vartheta} + \frac{4}{k\tau}} \quad (31)$$

Now we choose as new variables:

$$a f_v - \beta f_{v+1} = \chi_v.$$

This substitution does not yield the accurate coefficients for f_1^2 and f_n^2 for, in order to get n quantities χ , we have to take as one of the new variables $\chi_n = a f_n - \beta f_1$; so we introduce moreover a term $2 a \beta f_1 f_n$ which does not occur in the exponent. As however the exponent consists of an infinite number of infinitely small terms,

these three terms which have not the proper coefficients will be of little importance.

These new variables are now to be introduced into equation (27). Yet it is not necessary to execute the substitution completely, for, as we have only to determine the sum of the coefficients of the squares χ_v^2 , we may leave the coefficients of the products $\chi_v \chi_{v'}$ out of account. In the first place we have to express the old variables f in the new variables χ . We have:

$$\begin{aligned}\chi_1 &= \alpha f_1 - \beta f_2 \\ \chi_2 &= \alpha f_2 - \beta f_3 \\ \chi_3 &= \alpha f_3 - \beta f_4\end{aligned}$$

From this follows:

$$f_1 \begin{vmatrix} \alpha - \beta & 0 & 0 & 0 \dots & 0 \\ 0 & \alpha - \beta & 0 & 0 \dots & 0 \\ 0 & 0 & \alpha - \beta & 0 \dots & 0 \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ -\beta & 0 & 0 & 0 & \alpha \end{vmatrix} = \begin{vmatrix} \chi_1 - \beta & 0 & 0 & 0 \dots & 0 \\ \chi_2 & \alpha - \beta & 0 & 0 \dots & 0 \\ \chi_3 & 0 & \alpha - \beta & 0 \dots & 0 \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \chi_n & 0 & 0 & 0 & \alpha \end{vmatrix}$$

$$\text{or } f_1 (\alpha^n - \beta^n) = \chi_1 \alpha^{n-1} + \chi_2 \alpha^{n-2} \beta + \chi_3 \alpha^{n-3} \beta^2 + \dots \chi_n \beta^{n-1}$$

In the same way we find for f_v

$$\begin{aligned}f_v (\alpha^n - \beta^n) &= \chi_v \alpha^{n-1} + \chi_{v+1} \alpha^{n-2} \beta + \chi_{v+2} \alpha^{n-3} \beta^2 \dots \\ &\dots \chi_n \alpha^{n-1} \beta^{n-v} + \chi_1 \alpha^{v-2} \beta^{n-v+1} \dots \chi_{v-1} \beta^{n-1} \dots\end{aligned} \quad (32)$$

In determining the products $f_v f_{v'}$ we shall always suppose that $v' > v$, and so we shall integrate v between the limits 0 and v' ; v' between the limits 0 and ∞ . In this way we get only one half of the quantity we have to determine. In order to find the amount contributed by the product $f_v f_{v'} \cos(v' - v) \tau p$ to the coefficient of χ_r^2 , we have to distinguish three different cases:

1st. $0 < r < v$. Then the coefficient has the following form:

$$\alpha^{v+v'-2r-2} \beta^{2n+2r-v-v'} \cos(v' - v) \tau p$$

2nd. $v < r < v'$. Then:

$$\alpha^{n+v+v'-2r-2} \beta^{n+2r-v-v'} \cos(v' - v) \tau p$$

3rd. $v' < r < n$. Then:

$$\alpha^{2n+v+v'-2r-2} \beta^{2r-v-v'} \cos(v' - v) \tau p.$$

We have to seek the sum of these quantities, when r gets successively the value of all integers 1st. between 0 and v , 2nd. between v and v' and 3rd. between v' and n . v has all values between 0 and v' , and v' those between 0 and n . We may write these sums in the form of integrals, if we put:

$$\begin{aligned}\tau v &= u & \tau v' &= u' & \tau r &= w & \tau n &= t_1 \\ \alpha^{1/\tau} &= a & \text{and} & & \beta^{1/\tau} &= b.\end{aligned}$$

The integration according to w may directly be executed. It yields for the three cases:

$$\int \frac{a^{-2w}}{b} dw = \frac{-1}{2l} \frac{a^{-2w}}{b}$$

If we substitute in this equation for each case the proper limits and if we then add the results for the three cases, then we get:

$$\int_0^{t_1} \int_0^{u'} \frac{-1}{2l} \frac{a}{b} [b^{2t_1} \{ a^{-u+u'} b^{u+u'} - a^{u+u'} b^{-u-u'} \} + a^{t_1} b^{t_1} \{ a^{u-u'} b^{-u+u'} - a^{-u+u'} b^{u-u'} \} + a^{2t_1} \{ a^{u+u'-2t_1} b^{-u-u'+2t_1} - a^{u-u'} b^{-u+u'} \}] \cos p(u'-u) du du'.$$

In the exponent of a we have neglected the term 2τ as it is small compared with the other terms. If we arrange the terms in another way and again suppress the constant factors we may write the integral in the following form:

$$\begin{aligned} & \int_0^{t_1} \int_0^{u'} (a^{t_1} b^{t_1} - a^{2t_1}) \left(\frac{a}{b}\right)^{-u'} \left(\frac{a}{b}\right)^u \cos p(u'-u) du du' + \\ & + \int_0^{t_1} \int_0^{u'} (b^{2t_1} - a^{t_1} b^{t_1}) \left(\frac{a}{b}\right)^{u'} \left(\frac{a}{b}\right)^{-u} \cos p(u'-u) du du' . . . \quad (33) \end{aligned}$$

Integrating partially we find:

$$\begin{aligned} & \int_0^{u_1} \left(\frac{a}{b}\right)^u \cos p(u'-u) du = \frac{1}{l \frac{a}{b}} \left[\left(\frac{a}{b}\right)^u \cos p(u'-u) \right]_0^{u_1} - \frac{p}{l \frac{a}{b}} \int_0^{u_1} \left(\frac{a}{b}\right)^u \sin p(u'-u) du = \\ & = \frac{1}{b \frac{a}{b}} \left[\left(\frac{a}{b}\right)^u \cos p(u'-u) \right]_0^{u_1} - \frac{p}{l^2 \frac{a}{b}} \left[\left(\frac{a}{b}\right)^u \sin p(u'-u) \right]_0^{u_1} - \frac{p^2}{l^2 \frac{a}{b}} \int_0^{u_1} \left(\frac{a}{b}\right)^u \cos p(u'-u) du \end{aligned}$$

From which follows:

$$\int_0^{u_1} \left(\frac{a}{b}\right)^u \cos p(u'-u) du = \frac{l \frac{a}{b} \left\{ \left(\frac{a}{b}\right)^{u'} - \cos pu' \right\} - p \sin pu'}{l^2 \frac{a}{b} + p^2}$$

In the same way we have:

$$\int_0^{u_1} \left(\frac{a}{b}\right)^{-u} \cos p(u'-u) du = \frac{l \frac{a}{b} \left\{ -\left(\frac{a}{b}\right)^{-u'} + \cos pu' \right\} - p \sin pu'}{l^2 \frac{a}{b} + p^2}$$

If we introduce these values into expression (33), it assumes the following form:

$$\frac{1}{l^2 \frac{a}{b} + p^2} \int_0^{t_1} \left[(a^{t_1} - b^{t_1}) l \frac{a}{b} - \left\{ a^{t_1} \left(\frac{a}{b} \right)^{-u'} - b^{t_1} \left(\frac{a}{b} \right)^{u'} \right\} l \frac{a}{p} \cos pu' - \right. \\ \left. - \left\{ a^{t_1} \left(\frac{a}{b} \right)^{-u'} - b^{t_1} \left(\frac{a}{b} \right)^{u'} \right\} p \sin pu' \right] du'$$

Integrating this equation we get:

$$\frac{1}{l^2 \frac{a}{b} + p^2} \left[(a^{t_1} - b^{t_1}) l \frac{a}{b} t_1 - (a^{t_1} - b^{t_1}) l \frac{a}{b} p - (a^{t_1} + b^{t_1}) l^2 \frac{a}{b} + \right. \\ \left. + (a^{t_1} + b^{t_1}) l^2 \frac{a}{b} (\sin pt_1 + \cos pt_1) + (a^{t_1} - b^{t_1}) p l \frac{a}{b} (\sin pt_1 - \cos pt_1) \right],$$

The fact that the terms with $\sin pt_1$ and $\cos pt_1$ occur, shows that the distribution depends on t_1 . We might have expected this, specially as we have chosen $\alpha f_n - \beta f_1$ as one of new variables for the substitution and therefore introduced the condition that f_1 and f_n have about the same value. If however we take a considerable value for t_1 then the term $(a^{t_1} - b^{t_1}) l \frac{a}{b} t_1$ will have decisive influence. If we now consider a region of the spectrum of some, though it be an extremely small extension and not a rigorously simple wave, then we have to admit slight variations in the value of p . The terms $\sin pt_1$ and $\cos pt_1$ will then have alternately the positive and the negative sign and yield zero on an average.

If t_1 has a sufficiently great value then the course of the function is principally determined by the factor $\frac{1}{l^2 \frac{a}{b} + p^2}$. This expression does

not present a well defined maximum value, but it has its greatest value for $p = 0$ (i.e. for infinite wave-lengths), it decreases gradually with increasing p and is zero for $p = \infty$ (i.e. for infinitely small wave-lengths).

So this equation does not at all represent the distribution of black radiation. I only communicate these calculations in order to show that equations analogous to (8) or (8a) determine in fact a distribution of the energy over the different periods and to indicate a method for analysing such like equations.

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(Continued from pag. 21).

If the temperature is so low that there is no question of critical phenomena, and if therefore both liquid sheet and vapour sheet cover the whole triangle, v_{21} is for all points either positive or negative, and the given rules for the displacement of the curves of equal pressure will therefore be followed by all points of these curves. If on the other hand the temperature is chosen so high, that the surface of saturation does not cover any longer the whole triangle, and if therefore the liquid sheet and the vapour sheet pass into each other above a certain locus in the triangle, v_{21} vanishes for the phases represented by this locus.

We may form an idea of the shape of the surface of saturation with the aid of fig. 11 (Cont. II, p. 135). Let us imagine that this figure represents a section by the vertical plane which contains the X -axis of the triangle and let us take a similar section by the vertical plane which contains the Y -axis. The value of T is then chosen such that $T > (T_{cr})_2$, and also $T > (T_{cr})_3$. In the figure mentioned P is the point, where a vertical tangent may be drawn, so this point represents a phasis which is in critical point-of-contact circumstance, and for which $v_{21} = 0$. The point C represents the plaitpoint. If we now imagine different planes which contain the axis erected in the point O normal to the plane of the triangle, these planes will cut the surface of saturation, and the sections will be analogous figures, which however change their shape fluently from that which they have in the POX -plane to that which they have in the POY -plane. If the pressure is lower than the lowest pressure of the points P , the two branches of the curves of equal pressure are perfectly separated lines which, if the pressure is increased, will be displaced according to the rules given above. If however the pressure has risen till the pressure of a point P has been reached, then the two branches are still separated, but on the vapour branch occurs a point for which $v_{21} = 0$. Such a point is not displaced when the pressure increases. The locus of these points forms the limit of the mixtures which may be splitted up into two phases at the given temperature. From a geometrical point of view it is the envelope of the projections of the horizontal sections of the surface of saturation, or the envelope of the projections of the curves of equal pressure. If the pressure has been increased till it has attained the value of the lowest of the pressures of the point C , then the two branches of the curves of equal pressure pass continuously into one

another. But if we continue to call those phases represented by the lower sheet, vapour phases, and those phases represented by the higher sheet, liquid phases, then the vapour phases do not reach the point, where the connection of the two branches has taken place (the plaitpoint), but only the point where the value of v_{21} is zero, i. e. the point, where two successive curves of equal pressure intersect. For all points lying on one of the sides of that point of intersection, — e.g. on the side where the plaitpoint occurs, — v_{21} is positive.

These points will be displaced towards the conjugated point, when the pressure is increased; all points on the other side of the point of intersection will move away from the points, representing coexisting phases. If we, therefore, continue to use the expressions "liquid phasis" and "vapour phasis" with the same meaning as we have done till now, we must say that for points between the plaitpoint and the point for which $v_{21} = 0$ two liquid phases coexist. If for the two pairs of the ternary system we had a course of the pressure as is represented in Cont. II, p. 135, fig. 12, the above rules would continue to hold; but in this case we find a series of vapour phases coexisting with vapour phases between the plaitpoint and the point, for which $v_{21} = 0$. For these points we have then retrograde condensation of the second kind. We may expect that it will be easier to observe this phenomenon for a ternary system, than for a binary one. In order that retrograde condensation may be easily observed a rather great distance between the two sheets of the surface of saturation is required; and the distance between the sheets will be more considerable in the middle than at the ends, where we have to deal with a binary mixture, because the requirements for stability and coexistence for a ternary mixture are stricter than those for a binary mixture (See Vol. IV, p. 577). But then we have to avoid the case that a real maximum pressure occurs, for in that case we have also in the middle of the figure a point in which the two sheets touch each other.

c. Curves of slope and nodal envelopes.

If for a binary mixture we have construed the curves $p = f(v_1)$ and $p = f(v_2)$, we have at the same time answered the question, what phases may coexist with each other. Every line parallel to the X-axis joins a pair of coexisting phases. If on the other hand we have construed the two sheets of the surface of saturation for a ternary system, this is not sufficient in order to answer the question which

phasis coexists with a given phasis. It is true that we know that the pressure must be the same, and that therefore the second phasis will be found on the other sheet at the same height as the first phasis, but as the section of the second sheet by a plane at a height equal to p is a curve and not a point, the question is not yet perfectly determined. Therefore, besides the series of curves of equal pressure, which are already given as the points which have the same height, still another series of curves must be traced on the surface of saturation which pass from lower to higher pressure and whose properties enable us to answer the question, which phasis of one of the sheets corresponds with a given phasis of the other sheet. We will again begin with treating the simplest case, in which maximum-pressures are excluded, as well for the pairs of components of which the ternary system consists, as for the ternary system itself, so the case for which the lowest pressure is equal to p_1 and the highest to p_3 . The question is then, what systems of curves, starting at the point where the pressure has the lowest value and ending in the point where the pressure has the highest value, may be traced on one of the sheets or on both sheets of the surface of saturation which enable us to find, what phases coexist with each other. Such a system of curves will be found in the course of a person who would climb the inclined sheet, e. g. the liquid sheet, always moving in such a direction that he has the phasis, coexisting with the point, where he is at the moment, just in front of him. If we now project the tangent to the way which he has followed on a horizontal plane, the point in which this projection cuts the vapour sheet will indicate the coexisting phasis. The projection of such curves on the plane of triangle OXY has therefore the property that the tangent passes through the conjugate point, and is therefore the chord, joining the points 1 and 2; from this follows again that these projections are the envelopes of these chords. If therefore in the plane of the triangle we have drawn the two branches of the curves of equal pressure, and if we have joined a pair of nodes by a chord, an element of the curve in question will be represented by an infinitely small part of this chord. Let the point from which we start represent a liquid phasis and be its coordinates x_1 and y_1 . The projections of the element of the way followed are then the quantities dx_1 and dy_1 . At the end of the elementary way the second phasis is also changed, of course, and the consequence of this will be that we have to follow a curve. But the direction of the infinitely small way will always be the same as that of the chord joining the nodes; and the differential equation will therefore be given by:

$$\frac{dx_1}{x_2 - x_1} = \frac{dy_1}{y_2 - y_1}.$$

For these curves on the surface of saturation I have chosen the name of "curves of slope". This series of curves begins and ends with the following curves: 1st the curve $p = f(y_1)$ for the pair (1, 3), and 2nd the curve consisting of a $p = f(x_1)$ part for the pair (1, 2) and of a corresponding part for the pair (2, 3). If we draw these curves on the vapour sheet, we must imagine that we descend instead of ascending. For the projection of these curves on the plane of the triangle I have chosen the name of "nodal envelope". The outmost curves of this series are: 1st one of the sides of the triangle, adjacent to the right angle, namely that one corresponding to the third component, and 2nd a line consisting of the other side adjacent to the right angle and the hypotenuse of the triangle.

For the solution of the differential equation of these curves it is required that we may express x_2 and y_2 in x_1 and y_1 . This is possible (p. 7) when the second phasis is a rare gas phasis, if we namely assume the functions μ'_{x_1} and μ'_{y_1} to be known. For that case the equation we have to integrate may be written:

$$\frac{dx_1}{x_1 \{ (1-x_1)(e^{\mu'_{x_1}}-1) - y_1(e^{\mu'_{y_1}}-1) \}} = \frac{dy_1}{y_1 \{ (1-y_1)(e^{\mu'_{y_1}}-1) - x_1(e^{\mu'_{x_1}}-1) \}},$$

or

$$\frac{dx_1}{x_1 \{ (1-x_1-y_1)(e^{\mu'_{x_1}}-1) + y_1(e^{\mu'_{x_1}}-e^{\mu'_{y_1}}) \}} = \frac{dy_1}{y_1 \{ (1-x_1-y_1)(e^{\mu'_{y_1}}-1) - x_1(e^{\mu'_{x_1}}-e^{\mu'_{y_1}}) \}},$$

$$\text{or } \frac{dx_1}{x_1} (e^{\mu'_{y_1}}-1) - \frac{dy_1}{y_1} (e^{\mu'_{x_1}}-1) = (e^{\mu'_{y_1}}-e^{\mu'_{x_1}}) \frac{d(1-x_1-y_1)}{1-x_1-y_1},$$

$$\text{or } (e^{\mu'_{y_1}}-1) \left\{ \frac{dx_1}{x_1} - \frac{d(1-x_1-y_1)}{1-x_1-y_1} \right\} = (e^{\mu'_{x_1}}-1) \left\{ \frac{dy_1}{y_1} - \frac{d(1-x_1-y_1)}{1-x_1-y_1} \right\}.$$

The last equation may also be written as follows:

$$(e^{\mu'_{y_1}}-1) d \log \frac{x_1}{1-x_1-y_1} = (e^{\mu'_{x_1}}-1) d \log \frac{y_1}{1-x_1-y_1}.$$

For the case that the liquid sheet is a plane, $e^{\mu'_{y_1}}-1$ and $e^{\mu'_{x_1}}-1$ are constant, and equal to $\frac{p_3-p_1}{p_1}$ and $\frac{p_2-p_1}{p_1}$ and so the equation of the nodal envelope will be given by:

$$\left(\frac{x_1}{1-x_1-y_1} \right)^{\frac{p_3-p_1}{p_1}} = C \left(\frac{y_1}{1-x_1-y_1} \right)^{\frac{p_2-p_1}{p_1}},$$

$$\text{or} \quad x_1^{\left(\frac{p_3-p_1}{p_1}\right)} = C y_1^{\left(\frac{p_2-p_1}{p_1}\right)} (1-x_1-y_1)^{\left(\frac{p_3-p_2}{p_1}\right)},$$

an equation in which all exponents are positive as appears from the values of p_1 , p_2 and p_3 .

For $C=0$ this equation is satisfied by $x_1=0$ and therefore the nodal envelope coincides with the Y -axis. For $C=\infty$ either y_1 or $1-x_1-y_1$ is zero, and for this value of C the nodal envelope coincides with the X -axis and the hypotenuse. For the special case, for which $p_2=2p_1$ and $p_3=3p_1$ the equation assumes the following shape:

$$x_1^2 = C y_1 (1-x_1-y_1).$$

This is the equation of a conic section which touches the X -axis and the hypotenuse in the points in which they cut the Y -axis. Whatever the values of p_1 , p_2 and p_3 may be, the curve will touch the X -axis and the hypotenuse in the points mentioned, if only the condition $p_1 < p_2 < p_3$ be satisfied, and the same would hold true if on the other hand $p_1 > p_2 > p_3$ be fulfilled. The nodal envelope for which $C=0$ will of course be an exception to this rule.

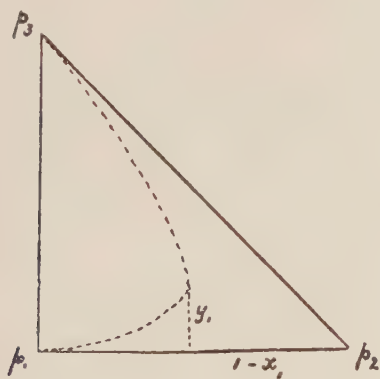


Fig. 13.

For the locus of the points where the tangent of the nodal envelope is parallel to the Y -axis for instance, we find in the case that μ'_{x_1} and μ'_{y_1} are constant a right line passing through the intersection of the X -axis and the hypotenuse. For $\frac{dy_1}{dx_1} = \infty$ for such points and so $dx_1=0$. But then also $x_2-x_1=0$. As follows from the equations (p. 11).

$$\frac{x_2-x_1}{x_1} = \frac{(1-x_1)(e^{\mu'_{x_1}}-1) - y_1(e^{\mu'_{y_1}}-1)}{1 + x_1(e^{\mu'_{x_1}}-1) + y_1(e^{\mu'_{y_1}}-1)}$$

and

$$\frac{y_2 - y_1}{y_1} = \frac{(1 - y_1)(e^{\mu' y_1} - 1) - x_1(e^{\mu' x_1} - 1)}{1 + x_1(e^{\mu' x_1} - 1) + y_1(e^{\mu' y_1} - 1)}$$

we have:

$$x_2 - x_1 = 0$$

if

$$1 - x_1 = y_1 \frac{e^{\mu' y_1} - 1}{e^{\mu' x_1} - 1}$$

This equation represents a right line, if the factor of y_1 is constant, and it yields $x_1 = 1$ if $y_1 = 0$. If the surface of saturation is a plane, i.e. if $e^{\mu' x_1} = \frac{p_2}{p_1}$ and $e^{\mu' y_1} = \frac{p_3}{p_1}$, then the equation of this right line is:

$$1 - x_1 = y_1 \frac{p_3 - p_1}{p_2 - p_1}.$$

This right line coincides with the liquid branch of the projection of the curve of the pressure p_2 . (See our previous communication, p. 14).

If μ'_{x_1} and μ'_{y_1} are not constant, i.e. if the factor of y_1 is variable, then the locus of the points for which $x_2 - x_1 = 0$ is of course not straight, but it will be a curve, which, however, if the condition $\mu'_{y_1} > \mu'_{x_1}$ continues to be satisfied, will start from the same angle of the triangle. In this case the line for which $x_2 - x_1 = 0$ does no longer coincide with the line for which the pressure is equal to p_2 . If we put in equation (7) of p. 12.

$$1 - x_1 = y_1 \frac{e^{\mu' y_1} - 1}{e^{\mu' x_1} - 1}$$

then we find :

$$\log \frac{p}{MRT} = \mu_{x_1 y_1} + (1 - x_1) \mu'_{x_1} - y_1 \mu'_{y_1} - 1.$$

If we denote the value of μ for $x = 1$ and $y = 0$ by μ_{10} , then we have:

$$\log \frac{p}{p_2} = \mu_{x_1 y_1} + (1 - x_1) \mu'_{x_1} - y_1 \mu'_{y_1} - \mu_{10}.$$

The second member of this equation represents the distance between the point of intersection of the tangential plane to the μ -surface and the vertical axis of the second component, and between the ordinate μ_{10} . If the whole surface lies below the tangential plane, as is probable, then the second member is positive and $p > p_2$, and the difference between p and p_2 increases, if the point of intersection

lies at a greater distance from the second component, and if the deviation of the surface μ from a plane surface is more considerable.

The succession of the values of the pressures p_1 , p_2 and p_3 involves that the condition $y_2 - y_1 = 0$, which would lead to:

$$1 - y_1 = x_1 \frac{e^{\mu'x_1} - 1}{e^{\mu'y_1} - 1}$$

cannot be fulfilled, for in that case the factor of x_1 would be less than unity, and the equation:

$$1 - y_1 = x_1 \frac{e^{\mu'x_1} - 1}{e^{\mu'y_1} - 1}$$

with constant value of μ'_{x_1} and μ'_{y_1} would then in fact represent a line through the summit of the triangle; but a line outside the triangle. But we will return to this condition presently.

These nodal envelopes have an analogous significance as that of the lines of force in the magnetic field. In the same way as the tangents of the lines of force determine the direction of the force, but not its intensity, so the tangents of the envelopes determine the direction in which the second phasis is to be found; but they do not indicate the distance between the points 1 and 2. This distance, however, is perfectly determined if also both branches of the curves of equal pressure and triangle OXV are drawn. Then we find the second phasis which coexists with a given liquid phasis, by drawing in the point representing the liquid phasis the tangent to the nodal envelope of that point; the point of intersection of this tangent and the vapour branch for the pressure of the liquid phasis represents the second phasis. If we do this for all points of the same nodal envelope then we get a new locus, which we may call conjugated curve of the nodal envelope. In order to give the equation of this conjugated curve we must be able to express x_1 and y_1 as functions of x_2 and y_2 and we must substitute these functions in the equation of the envelope. In general, however, we are not able to do this, not even in the case that the second phasis is a rare gas phasis. Only in the case that μ'_{x_1} and μ'_{y_1} may be considered as constants it can easily be executed. If we write the equation of the envelope as follows:

$$\left(\frac{x_1}{1 - x_1 - y_1} \right) (e^{\mu'y_1} - 1) = C \left(\frac{y_1}{1 - x_1 - y_1} \right) (e^{\mu'x_1} - 1),$$

which only may be admitted for constant value of μ'_{x_1} and μ'_{y_1} , and if we take into account that:

$$\frac{x_1}{1-x_1-y_1} = \frac{x_2 e^{-\mu' x_1}}{1-x_2-y_2}$$

and

$$\frac{y_1}{1-x_1-y_1} = \frac{x_2 e^{-\mu' y_1}}{1-x_2-y_2}$$

then the substitution into the equation of the envelope yields the following formula:

$$\left(\frac{x_2 e^{-\mu' x_1}}{1-x_2-y_2} \right) (e^{\mu' y_1} - 1) = C \left(\frac{y_2 e^{-\mu' y_1}}{1-x_2-y_2} \right) (e^{\mu' x_1} - 1),$$

or

$$\left(\frac{x_2}{1-x_2-y_2} \right) (e^{\mu' y_1} - 1) = C' \left(\frac{y_2}{1-x_2-y_2} \right) (e^{\mu' x_1} - 1).$$

From this follows that the conjugated curve of a nodal envelope of liquid phases, is, in the chosen circumstances again a nodal envelope, with another value of the constant, namely:

$$C' = C \left(\frac{p_2}{p_1} \right)^{\frac{p_3-p_1}{p_1}} \left(\frac{p_1}{p_3} \right)^{\frac{p_2-p_1}{p_1}}.$$

If $p_1 < p_2 < p_3$, the factor of C is greater than unity and the conjugated curve is therefore to be found nearer the hypotenuse. Only in the case that $p_2 = p_3$ we have $C' = C$; but then the system is only apparently a ternary one, and the envelope degenerates into a straight line with the equation:

$$x = Cy:$$

It appears therefore that the conjugated curve in this case always coincides with the envelope.

We might also have considered the nodal envelope for vapour phases. Then we consider the projection of the way which we should follow, if we descend on the vapour sheet from the point where the pressure has the highest value towards the point, where it has the lowest value, always moving in such a direction that we have the liquid phasis just in front. We find the equation of this curve if we express the values of x_1 and of y_1 as functions of x_2 and y_2 and if we substitute those functions into:

$$\frac{dx_2}{x_1 - x_2} = \frac{dy_2}{y_1 - y_2}$$

This is only possible if μ'_{x_1} and μ'_{y_1} are constant as we have already mentioned several times. With the aid of the equations:

$$\frac{x_1}{1-x_1-y_1} = \frac{x_2}{1-x_2-y_2} e^{-\mu' x_1}$$

and

$$\frac{y_1}{1-x_1-y_1} = \frac{y_2}{1-x_2-y_2} e^{-\mu' y_1},$$

we find a differential equation, which differs from the one treated p. 124 in so far that x_2 , y_2 , dx_2 and dy_2 are substituted for x_1 , y_1 , dx_1 and dy_1 , and that $-\mu'_{x_1}$ and $-\mu'_{y_1}$ are substituted for μ'_{x_1} and μ'_{y_1} . In the integral found there the same substitutions must of course be performed. So we find:

$$\left(\frac{x_2}{1-x_2-y_2} \right) (e^{-\mu'_{y_1}} - 1) = C \left(\frac{y_2}{1-x_2-y_2} \right) (e^{-\mu'_{x_1}} - 1)$$

or

$$\left(\frac{x_2}{1-x_2-y_2} \right)^{\left(\frac{p_1}{p_3} - 1 \right)} = C \left(\frac{y_2}{1-x_2-y_2} \right)^{\left(\frac{p_1}{p_2} - 1 \right)}$$

This equation may also be written in the following form:

$$x_2^{\frac{p_2}{p_3} - \frac{p_1}{p_3}} = C_2 y_2^{\frac{p_3}{p_2} - \frac{p_1}{p_2}} (1-x_2-y_2)^{\frac{p_3}{p_1} - \frac{p_2}{p_1}}$$

For $C_2=0$, we have also $x_2=0$, and the Y -axis is therefore the first of the envelopes, just as was the case for the liquid phases. For $C_2=\infty$ we have $y_2=0$ and $1-x_2-y_2=0$. The last of the envelopes is therefore also here the X -axis and the hypotenuse. Though the equation of the two series of envelopes is different, the course is in many respects analogous. These envelopes also touch the hypotenuse in their beginning and touch the X -axis in their final point. They have a tangent parallel to the Y -axis, and the locus of the points where this is the case, is found from the equation:

$$x_1 - x_2 = 0$$

or

$$1 - x_2 = y_2 \frac{1 - e^{-\mu'_{y_1}}}{1 - e^{-\mu'_{x_1}}}$$

or

$$1 - x_2 = y_2 \frac{p_2}{p_3} \frac{p_3 - p_1}{p_2 - p_1}.$$

This locus coincides with the vapour branch of the curve of pressure p_2 . This nodal envelope has a conjugated curve, which is again a nodal envelope with greater value of the constant, just as is the case for the liquid phases.

Before we proceed to the discussion of the nodal envelopes in more complicated cases, namely in those in which a maximum pressure occurs either on the sides of the triangle or for a point inside the triangle, we will make some general observations about peculiar points of these curves, which, however, only apply to the case that the second phasis is a rare gas phasis.

From the equation :

$$\frac{x_2}{1-x_2-y_2} = \frac{x_1}{1-x_1-y_1} e^{\mu'_{x_1}}$$

$$\frac{y_2}{1-x_2-y_2} = \frac{y_1}{1-x_1-y_1} e^{\mu'_{y_1}}$$

we deduce that the nodal envelopes have tangents which pass through the angles of the triangle, if either μ'_{x_1} , or μ'_{y_1} , or $\mu'_{y_1} - \mu'_{x_1}$ are equal to zero. The tangent contains the angle representing the third component, if $\mu'_{x_1} = 0$; that representing the second component if $\mu'_{y_1} = 0$; and that for the first component if $\mu'_{y_1} = \mu'_{x_1}$.

The conditions that a tangent of the envelope is parallel to one of the sides of the triangle may be deduced from the values of $x_2 - x_1$ and $y_2 - y_1$. So from $x_2 - x_1 = 0$ follows the condition that the tangent is parallel to the side of the first and the third components. This condition has the following form:

$$\frac{y_1}{1 - x_1} = \frac{e^{\mu'_{x_1}} - 1}{e^{\mu'_{y_1}} - 1}.$$

Now $\frac{y_1}{1 - x_1} = \tan \alpha$, where α represents the angle enclosed between the radius vector drawn from the second component, and the X -axis. As α must be less than 45° , we get for the condition for the existence of points where the tangent is parallel to the Y -axis:

$$\tan \alpha = \frac{e^{\mu'_{x_1}} - 1}{e^{\mu'_{y_1}} - 1}$$

and $\mu'_{x_1} < \mu'_{y_1}$, if both are positive.

The condition that the tangent is parallel to the X -axis may be derived from $y_2 - y_1 = 0$ and has the following form:

$$\frac{x_1}{1 - y_1} = \frac{e^{\mu'_{y_1}} - 1}{e^{\mu'_{x_1}} - 1}$$

As $\frac{x_1}{1 - y_1} = \tan \beta$, where β represents the angle, enclosed between the radius vector drawn from the third component, and the Y -axis, we may write this condition as follows:

$$\tan \beta = \frac{e^{\mu'_{y_1}} - 1}{e^{\mu'_{x_1}} - 1}$$

and $\mu'_{x_1} > \mu'_{y_1}$, if both are positive.

The condition that the tangent is parallel to the hypotenuse may be derived from:

$$\frac{y_2 - y_1}{x_2 - x_1} = -1.$$

From this we deduce:

$$\frac{y_1}{x_1} = - \frac{e^{\mu' x_1} - 1}{e^{\mu' y_1} - 1}$$

Therefore a tangent of the nodal envelope parallel to the hypotenuse can only occur in the case that μ'_{x_1} and μ'_{y_1} have different sign.

All these relations apply only to the case that μ'_{x_2} and μ'_{y_2} may be equated to zero; and the given rules will require corrections when the temperature is increased and approaches one of the critical temperatures. If T has reached a value higher than $(T'_{cr})_3$ for instance, and consequently the surface of saturation does not cover the whole triangle any more, the envelopes can no longer pass through the angle of the third component. Even without knowledge of the equation of the envelopes we can understand in the following way what peculiarity will then come into the shape of those curves. The surface of saturation has in the vertical plane containing the Y -axis, and also in that containing the hypotenuse still the shape of fig. 11, Cont. II. The first curve of slope lies in the first mentioned vertical plane and consists of that part of the p curve of the figure mentioned which extends to the maximum, i.e. to the point C . All other points of this pressure-curve, as well those between C and P as those forming the lower branch, represent coexisting phases and belong to the conjugated curve of this curve of slope. The last of these curves of slope lies above the X -axis and above the hypotenuse, but above the hypotenuse it also extends only to the projection of the point of maximum pressure. Every intermediate nodal envelope has initially the shape of fig. 13, has also still a vertical tangent, but ends in a point (the projection of a plaitpoint) before it has reached the locus which represents the limit of the points above which the surface of saturation extends. Above such a limiting point of the nodal envelope the curve of slope of which it is the projection has reached its highest point. Before the limiting point however the course has been modified. In order to discuss this modification we will derive the second derivative function, namely $\frac{d^2 y_1}{dx_1^2}$. From:

$$\frac{dy_1}{dx_1} = \frac{y_2 - y_1}{x_2 - x_1} \text{ follows}$$

$$\frac{d^2 y_1}{dx_1^2} dx_1 = \frac{(x_2 - x_1)(dy_2 - dy_1) - (y_2 - y_1)(dx_2 - dx_1)}{(x_2 - x_1)^2},$$

$$\text{or } \frac{d^2 y_1}{dx_1^2} dx_1 = \frac{(dy_2 - dy_1) - \frac{dy_1}{dx_1} (dx_2 - dx_1)}{(x_2 - x_1)}$$

$$\text{or } \frac{d^2 y_1}{dx_1^2} dx_1 = \frac{dy_2 - \frac{dy_1}{dx_1} dx_2}{(x_2 - x_1)}.$$

When we write it in this form we see that $\frac{d^2 y_1}{dx_1^2} = 0$ for that phasis for which dx_2 and dy_2 are zero, so for that phasis which coexists with the critical point of contact. If we write:

$$\frac{d^2 y_1}{dx_1^2} \frac{dx_1}{dx_2} = \frac{\frac{dy_2}{dx_2} - \frac{dy_1}{dx_1}}{(x_2 - x_1)},$$

then the value of $\frac{d^2 y_1}{dx_1^2}$ assumes for the plaitpoint, where $x_2 = x_1$,

and $\frac{dy_2}{dx_2} = \frac{dy_1}{dx_1}$ a shape which is indefinite. As, however, the points 1 and 2 are situated on opposite sides of the plaitpoint, and the point 2 must always lie on the tangent of 1, and the curve containing the points 1, the nodal envelope will present a point of inflection in the plaitpoint, i.e. in the point where it ends. The further continuation to the locus of the critical points of contact belongs to the conjugated curve, and this must reverse its course either abruptly or fluently, where it meets the locus mentioned.

Let us now pass to the discussion of the course of the nodal envelope in the case that a maximum pressure exists on one of the sides of the triangle. We shall suppose it to occur on the X -axis, so that the succession of the pressures is given by:

$$p_1 < p_2 < p_{12} < p_3.$$

If for a certain value of x_1 a maximum pressure occurs on the X -axis, then $x_2 - x_1 = 0$, and $y_1 = 0$; from which follows that for the point representing the phasis with maximum pressure we have:

$$\mu'_{x_1} = 0.$$

The locus, represented by $\mu'_{x_1} = 0$, (see our previous communication p. 9) cuts therefore one of the sides of the triangle adjacent to the right angle, namely that one which joins the angles representing the first and the second component. Inside this triangle therefore also a continuous series of points occurs for which this condition is satisfied. The shape of this locus cannot be determined without the knowledge of the equation of state. It might be derived from the equation on

p. 9, if T_{cr} and p_{cr} were known as functions of x and y . If we assume, that T_{cr} is proportional to $\frac{a}{b}$ and p_{cr} is proportional to $\frac{a}{b^2}$, as follows from the form of the equation of state I have adopted, then we see that $\mu'_{x_1} = 0$ in the case under consideration represents a feebly bent curve, which starting from the X -axis intersects either the Y -axis or the hypotenuse. Which of these lines will be cut depends on the values of $(T_{cr})_1$ and of $(T_{cr})_2$ and on the size of the molecules of the components 1 and 2. As intermediate case the curve $\mu'_{x_1} = 0$ might pass through the angle of the third component. In

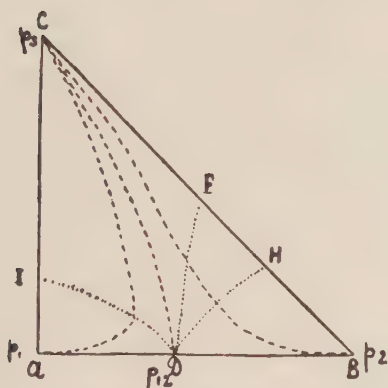


Fig. 14

fig. 14 I have represented it by curve DF , so I have assumed it to cut the hypotenuse. The area of the triangle may be divided into two parts according to the value of μ'_{x_1} . On the left of DF this quantity is positive; on the right of DF it is negative. As the quantity μ'_{y_1} does not change its sign in the case under consideration (the pressure not presenting a maximum on the lines AC and BC), the value of $\frac{\mu'_{x_1} - 1}{\mu'_{y_1} - 1}$ is positive on the left of DF , and negative on the right. The points in which the tangents to the nodal envelopes are vertical, can therefore only be found on the right of DF ; tangents parallel to the hypotenuse on the other hand can occur on the left of DF . On the line DF itself the tangents have a direction, passing through the point C . The curve DI represents the locus of the points whose tangent is vertical, and the curve DH that of the points whose tangent is parallel to the hypotenuse. We may easily form an idea of the course of the nodal envelopes themselves in main features if we consider them as slight modifications of the shape they should have if the curve DF were a straight line, directed towards the summit C . In that case namely the course of the envelopes in the left part is the same as that of fig. 13, — with the modification which follows from the fact that one of the sides, adjacent to the right angle is smaller than the other, — and in the right part it is symmetrical with fig. 13 with regard to the Y -axis, — with the modification which follows from the fact that an obtuse angle occurs instead of the right angle. In the left part $AD + DC$ is one of the outmost envelopes; in the right part $BD + DC$.

If also one of the other sides of the triangle presents a maximum pressure, e. g. the Y -axis, then we have to deal with still another locus: $\mu'_{y_1} = 0$. The circumstance whether the two curves $\mu'_{x_1} = 0$ and $\mu'_{y_1} = 0$ intersect or not decides whether for a ternary system a maximum pressure exists or not. The given rules concerning the peculiar points of the envelopes enable us in this and other cases to conclude to the course. But I will no longer dwell upon this subject. I consider the preceding discussion as sufficient to draw attention to the significance of these curves for the knowledge of a ternary system.

d. The addition of a third component to a given binary system.

If we have a binary system consisting of $1-x_0$ molecules of the first kind and x_0 molecules of the second kind, and we add to it a third component so that the final composition is given by $1-x-y$, x and y , then we have:

$$\frac{x}{1-x-y} = \frac{x_0}{1-x_0}.$$

From this relation we derive:

$$\frac{x}{x_0} = 1-y;$$

from which we conclude, that the points representing the ternary system lie on a straight line, which connects the summit of the rightangled triangle with that point on the opposite side that represents the composition of the binary system.

Taking into account the values of $\frac{\partial^2 \xi}{\partial x_1^2}$, $\frac{\partial^2 \xi}{\partial x_1 \partial y_1}$ and of $\frac{\partial^2 \xi}{\partial y_1^2}$ given on p. 5 and substituting the value $-x_0 dy_1$ for dx_1 , we find from formula II of p. 1.

$$\begin{aligned} \frac{v_{21}}{MRT} \frac{dp}{dy_1} = (x_2 - x_1) \left\{ \frac{-x_0(1-y)}{x_1(1-x_1-y_1)} + \frac{1}{1-x_1-y_1} + \mu''_{x_1 y_1} - x_0 \mu''_{x_1} \right\} + \\ + (y_2 - y_1) \left\{ \frac{-x_0}{1-x_1-y_1} + \frac{1-x_1}{y_1(1-x_1-y_1)} + \mu''_{y_1} - x_0 \mu''_{x_1 y_1} \right\}. \end{aligned}$$

This equation may be simplified to:

$$\frac{v_{21}}{MRT} \frac{dp}{dy_1} = (x_2 - x_1) \{ \mu''_{x_1 y_1} - x_0 \mu''_{x_1} \} + (y_2 - y_1) \left\{ \frac{1}{y_1(1-y_1)} + \mu''_{y_1} - x_0 \mu''_{x_1 y_1} \right\}.$$

In order to get the corresponding equation for the vapour phases, we must interchange the indices 1 and 2; it has the following form:

$$\frac{v_{21}}{MRT} \frac{dp}{dy_2} = (x_1 - x_2) \{ \mu''_{x_2 y_2} - x'_0 \mu''_{x_2} \} + (y_1 - y_2) \left\{ \frac{1}{y_2(1-y_2)} + \mu''_{y_2} - x'_0 \mu''_{x_2 y_2} \right\}$$

If the gas phases are very rarified the latter equation may be simplified to:

$$\frac{1}{p} \frac{dp}{dy_2} = \frac{y_2 - y_1}{y_2(1 - y_2)},$$

which form is identical with that which applies if a second component is added to a simple substance, and from which accordingly the quantity x'_0 has disappeared. This identity of the form of the *equation* does, however, not justify the conclusion that also the shape of the *curve* $p = f(y_2)$ will be identical. The same form of the *equation* applies also to a binary system, and yet it includes the great variety of curves which the pressure as a function of the composition of the vapour can present. All those differences in shape are to be ascribed to the different ways in which y_1 and y_2 depend upon each other. In the same way every plane section of the vapour sheet for a ternary system by a plane, normal to the plane of the triangle and passing through the summit, will be represented by this equation, though these sections may present an infinite variety of forms, which again may differ from those of a binary system. Yet we may make use of this equation and deduce some general properties from it. So e. g. $\frac{dp}{dy_2}$ will be zero if on the chosen section a point x_2, y_2 occurs for which

$$y_2 - y_1 = 0.$$

If the succession of the values of the pressures is $p_1 < p_2 < p_3$ this can never occur. In this discussion, however, we will think the succession to be changed according to the circumstances in order that we are not obliged to draw the section every time through another angle of the triangle. If the succession is $p_1 < p_3 < p_2$ a locus occurs indeed, for which $y_2 = y_1$ and this locus coincides with that for which the pressure of the vapour phases which occur on the chosen section is maximum or minimum. We might have expected a priori that in general a maximum or minimum would be found on the section which passes through the angle for the component whose pressure lies between those of the other components, and which cuts the opposite side in a point with the same pressure. This maximum or minimum will, however, not have the same significance as that of a binary system. For in the case of a binary system the composition of the vapour is the same as that of the liquid phasis; for a ternary system only y_1 and y_2 are equal, but x_1 and x_2 differ. In such a point the pressure of the liquid phasis is not equal to that of the vapour phasis — as is the case with the maximum pressure of a binary system, — but the pressure of

the liquid is higher than that of the vapour. The two sheets do not touch one another in such points. It is true that the pressure for a point conjugated to such a point is the same, but $\frac{dp}{dy_1}$ is different from zero, as appears from the equation for $\frac{dp}{dy_1}$.

If we substitute in this equation $y_1 = y_2$, we find:

$$\frac{1}{p} \frac{dp}{dy_1} = (x_2 - x_1) \{ \mu''_{x_1 y_1} - x \mu''_{x_1} \}.$$

The factor $x_2 - x_1$, which also may be written $\frac{d\mu'_{x_1}}{dy_1}$ depends on the curvature of the μ -surface, and in all cases in which the surface is only slightly bent it will have only a small value; but only in very special cases it will be rigorously zero. In general therefore we may assume, that this locus of the maximum liquid pressures does not deviate much from the locus for which $y_2 - y_1 = 0$. If the projections of the curves of equal pressure are drawn, the points of maximum pressure and the sections discussed by us are of course immediately to be determined, by tracing the tangents, passing through the angles of the triangle.

The value of $\frac{v_{21}}{MRT} \frac{dp}{dy_1}$ assumes exactly the same shape it has for a binary system if either $(x_1 - x_2)$ or $\frac{d\mu_{x_1}}{dy_1}$ are zero. The value of $x_2 - x_1$ vanishes in the first place if the quantity we have denoted by x_0 is zero, and in the second place if it is equal to unity. But in these cases we are really dealing with binary systems; in the first case with the pair 1,3 and in the second with the pair 2,3. In the first case we have:

$$\frac{v_{21}}{MRT} \frac{dp}{dy_1} = (y_2 - y_1) \left\{ \frac{1}{y_1(1-y_1)} + \mu''_{y_1} \right\}$$

and in the second case, if

$$1 - x_2 - y_2 = 1 - x_1 - y_1, \text{ or } x_2 - x_1 = -(y_2 - y_1):$$

$$\frac{v_{21}}{MRT} \frac{dp}{dy_1} = (y_2 - y_1) \left\{ \frac{1}{y_1(1-y_1)} + \mu''_{y_1} - 2\mu''_{x_1 y_1} + \mu''_{x_1} \right\}.$$

The quantity $\mu''_{y_1} - 2\mu''_{x_1 y_1} + \mu''_{x_1}$ has for the pair 2,3 the same signification as μ''_{y_1} , for the pair 1,3, as is easily understood.

The quantity $\frac{v_{21}}{MRT} \frac{dp}{dy_1}$ assumes also this simple shape in the very peculiar points, where $x_1 - x_2 = 0$ either inside the triangle or on one of its sides, and also in the points where $\frac{d\mu'_{x_1}}{dx_1}$ vanishes.

But in general the quantity $(x_2 - x_1)(\mu''_{x_1 y_1} - x_0 \mu''_{x_1})$ will cause a modification in the course of the value of the pressure which is very slight. The value of the pressure depending principally on the term $\frac{y_2 - y_1}{y_1(1 - y_1)}$.

We will consider more closely this last quantity, which represents the limiting value of $\frac{1}{p} \frac{dp}{dy_1}$ for $y_1 = 0$ or $y_1 = 1$, for a binary mixture and which for a ternary system is to be augmented with $(x_2 - x_1)_0 \frac{d\mu'_{x_1}}{dy_1}$.

We have found before the following value for $\frac{y_2 - y_1}{y_1}$:

$$\frac{y_2 - y_1}{y_1} = \frac{(1 - y_1)(e^{\mu'_{y_1}} - 1) - x_1(e^{\mu'_{x_1}} - 1)}{(1 - x_1 - y_1) + x_1 e^{\mu'_{x_1}} + y_1 e^{\mu'_{y_1}}},$$

From this value we deduce, if we set $y_1 = 0$ and $x_1 = x_0$

$$\frac{y_2 - y_1}{y_1(1 - y_1)} = \frac{(e^{\mu'_{y_1}} - 1) - x_0(e^{\mu'_{x_1}} - 1)}{1 + x_0(e^{\mu'_{x_1}} - 1)} = \frac{e^{\mu'_{y_1}}}{1 - x_0 + x_0 e^{\mu'_{x_1}}} - 1$$

where μ'_{x_1} and μ'_{y_1} have the values they have in the point whose coordinates are $x_1 = x_0$ and $y_1 = 0$. This value, which for $x_0 = 0$ is equal to $e^{\mu'_{y_1}} - 1$, has for $x_0 = 1$ the final value $e^{\mu'_{y_1} - \mu'_{x_1}} - 1$, and varies fluently with increasing x_0 ; and now the way in which $\frac{1}{p} \frac{dp}{dy_1}$ varies depends upon the relation between μ'_{y_1} and μ'_{x_1} . This value may have reversed its sign, either from negative to positive or from positive to negative. The quantity $\mu'_{y_1} - \mu'_{x_1}$ represents the variation of μ for the motion along the hypotenuse towards the summit of the triangle in the same way as μ'_{y_1} represents the variation for the motion along the Y -axis towards the summit. If therefore T_{cr} for the summit is lower than $(T_{cr})_1$, then μ'_{y_1} is positive, and if T_{cr} for the summit is higher than $(T_{cr})_2$ then $\mu'_{y_1} - \mu'_{x_1}$ is negative.

It is not superfluous to point out in how high a degree the value of $\frac{1}{p} \frac{dp}{dy_1}$ depends on the value of μ'_{y_1} , if it represents the initial direction of a curve of equal pressure for a binary system. According to our former observations this value is equal to $e^{\mu'_{y_1}} - 1$. If we also draw the vapour curve, then $\frac{1}{p} \frac{dp}{dy_2} = \frac{y_2 - y_1}{y_2}$, and so it is equal to:

$\frac{e^{\mu'_{y_1}} - 1}{e^{\mu'_{y_1}}} = 1 - e^{-\mu'_{y_1}}$ If we draw moreover the curve of the double

points then we have $\frac{dp}{p dy} = \mu'_{y_1}$. For the case that $\mu'_{y_1} = 0$ we always

find zero as well for the value of $\frac{1}{p} \frac{dp}{dy_1}$ as for $\frac{1}{p} \frac{dp}{dy_2}$ and $\frac{1}{p} \frac{dp}{dy}$.

If μ'_{y_1} is positive, the three lines ascend, and they descend if μ'_{y_1} is negative. If the value of μ'_{y_1} is very small, there is only a small difference in the slope of the three curves. But if μ'_{y_1} has not so very small a value, then there is a very great difference in the slope of the three curves, and the liquid branch ascends exceedingly fast.

$$\text{As} \quad \mu'_{y_1} = -\frac{f}{T} \frac{dT_{cr}}{dy_1} + \frac{d \log p_{cr}}{dy_1},$$

we shall have a great value μ'_{y_1} , if $\frac{dT_{cr}}{dy_1}$ has a considerable negative value, so if the T_{cr} of the second component is much lower, e.g. if we press a permanent gas into a liquid. As in general T_{cr} does not depend linearly on y_1 and $\frac{d \log p_{cr}}{dy_1}$ has a value differing from zero, we shall not find the accurate value for μ'_{y_1} , putting:

$$\mu'_{y_1} = \frac{f}{T} \{(T_{cr})_1 - (T_{cr})_2\}$$

but only a more or less approximated value. If we choose for the second component a substance whose T_{cr} is much lower than T and for the first component a substance, whose T_{cr} is much higher than T , we do not take an impossible value for μ'_{y_1} , if we give it the value 14 or 15 for

ordinary temperature. In that case $e^{\mu'_{y_1}}$ may in rough approximation be represented by 10^6 . If we might apply the results we have obtained, also in the case of water, though its behaviour is specially at low temperatures very abnormal, then we might form an idea of the degree of approximation by means of the absorption coefficients of gases solved in water.

According to our results we find for small values of y_1 , if we neglect the vapour pressure of the first component compared with the total pressure:

$$p = p_1 y_1 (e^{\mu'_{y_1}} - 1).$$

Here p_1 represents the vapour pressure of the first component. Further we have, denoting the absorption coefficient by α , and the molecular weight and the density of that component by m_1 and d_1 :

$$y_1 = \frac{m_1}{d_1} \frac{0,0013}{28,8} \alpha p.$$

If we neglect unity to $e^{\mu' y_1}$, we may derive from these two equations:

$$e^{\mu' y_1} = \frac{d_1}{m_1} \frac{28,8}{0,0013} \frac{1}{\alpha p_1}.$$

If we put in this equation $d_1 = 1$, $m_1 = 18$ and $p_1 = \frac{4.6}{760}$ Atmospheres, and $\alpha = 0,02$ as is the case for N_2 , then we find for μ'_{y_1} a value between 16 and 17. This result shows that the equation

$$\mu'_{y_1} = \frac{f}{273} \{(T_{cr})_w - (T_{cr})_{N_2}\}$$

does indeed hold as an approximation.

If we had chosen as second component a substance of small volatility and whose T_{cr} is much higher than $(T_{cr})_1$, then we might form an idea of the value of μ'_{y_1} by making use of the approximation:

$$\mu'_{y_1} = \frac{f}{T} \{(T_{cr})_1 - (T_{cr})_2\},$$

but then we should find a very great negative value for μ'_{y_1} and for $\frac{y_2}{y_1} = e^{\mu' y_1}$ a value which differs only slightly from zero.

When we add a third component to a binary system whose composition is determined by x_0 , then we have found for the value of $\frac{1}{p} \frac{dp}{dy_1}$, if y_1 is infinitely small:

$$\frac{1}{p} \frac{dp}{dy_1} = \frac{e^{\mu' y_1}}{1 - x_0 + x_0 e^{\mu x_1}} - 1 + (x_2 - x_1)_0 \{\mu''_{x_1 y_1} - x_0 \mu''_{x_1}\}.$$

The two branches of the pressure-curve of this section do not start in the same point and so they differ already from the beginning from those of a binary system. Only if $(x_2 - x_1)_0 = 0$ they start at the same point. But as the factor of $x_2 - x_1$ depends on the curvature of the μ surface the influence of this term may be neglected specially when μ'_{y_1} is great or when the curvature is considerable. So we find for the value of x_0 for which $\frac{1}{p} \frac{dp}{dy_1}$ vanishes approximately:

$$x_0 = \frac{e^{\mu' y_1} - 1}{e^{\mu' x_1} - 1}.$$

Only when $\mu'_{y_1} < \mu'_{x_1}$ this yields a possible value for x_0 at least if as well μ'_{y_1} as μ'_{x_1} are positive.

Geology. — "*Cambrian Erratic-blocks at Hemelum in the South-west of Frisia.*" By J. H. BONNEMA. (Communicated by Prof. J. W. MOILL).

To the East of Molkwerum, a railway-station between Leeuwarden and Stavoren, stretches a region that from a geological point of view is very remarkable; as was especially shown by the interesting researches of Dr. VAN CAPPELLE.¹⁾

The road first leads in a North-eastern direction to the village of Koudum, which is situated on elevated ground. As far as here the surface showed alluvial clay only; now we see for the first time diluvial formations. The outer part of this elevation consists of boulder-clay, whereas in two sand-pits it may be easily observed that preglacial layers form the inner part.

A little farther on, when the alluvial grounds are reached again, one comes to the Galama-dams. They are found on the Morra, according to the above-named author a bottommoraine-lake.

About a mile farther upward we again find diluvial soil, and on continuing our journey in the direction of Rijs we see, just before leaving Hemelum-Oldephaert and Noordwolde, and entering the domain belonging to Gaasterland, in a meadow to the right of the road a large pit 8 metres deep. From this pit for some years boulder-clay has been dug in behalf of the brick-works of the Comp. "Gaasterland", at a short distance, on the other side of the road.

As far as I know, these are the only brick-works in the Northern part of the Netherlands, where bricks are made of boulder-clay.

The boulder-clay, which forms a bottom-moraine here and which must be found very deep in the earth, is coloured blue-grey. Only quite near the humus-layer it has become red-brown, under the influence

¹⁾ VAN CAPPELLE, Les Escarpements du „Gaasterland” sur la côte meridionale de la Frise. Extrait du Bulletin de la Société Belge de géologie, de paléontologie et d'hydrologie 1889.

VAN CAPPELLE, Bijdrage tot de kennis van Frieslands bodem. II. Eenige mededeelingen betreffende de Gaasterlandsche kliffen. Tijdschrift v. h. Koninkl. Nederl. Aardrijksk. Genootschap. 1890.

VAN CAPPELLE, Bijdrage tot de kennis van Frieslands bodem. IV. Eenige mededeelingen over de diluviale heuvels in de gemeente Hemelum-Oldephaert en Noordwolde. Tijdschr. v. h. Kon. Nederl. Aardrijksk. Genootschap. 1892.

VAN CAPPELLE, Bijdrage tot de kennis van Frieslands bodem. V. Karteerling van 't diluvium van Gaasterland en Hemelum-Oldephaert en Noordwolde. Tijdschr. v. h. Kon. Nederl. Aardrijksk. Genootschap. 1895.

VAN CAPPELLE, Diluvialstudien im Südwesten von Friesland. Verhandelingen der Koninkl. Akad. v. Wetensch. te Amsterdam. 1895.

of the weather. It contains comparatively few erratic-blocks. They often show very fine glacier-scratches and are mostly of average size.

During the time when this opportunity of gathering erratic-blocks has presented itself, I have several times visited, from Leenwarden, this loam-pit. The result of these visits is that I brought home rather a large number of erratic-blocks (probably between 300 and 400).

The sedimentary ones are still here at present; after studying them I intend to present them to the Geological Institute at Groningen. The others, whose number is small compared with that of the sedimentary stones, have already been given to this Institute.

Though my collection is still small, it is large enough to confirm my opinion that our knowledge of our sedimentary erratic-blocks leaves much to be desired. I formed this opinion already after examining the erratic-blocks of Kloosterholt.¹⁾

In gathering erratic-blocks in the Gron. Hondsrug I had gradually come to the conclusion that our sedimentary ones almost exclusively originated from Silurian layers, and that the latter must have shown much resemblance to those of the Russian Baltic-sea provinces, perhaps are still to be found there. On getting acquainted with the erratic-blocks in the boulder-clay of Kloosterholt, however, I could not but see very soon that at any rate this rule does not hold good in all cases. In this place I often found pieces of older and younger formations, while corresponding stones occur as firm rocks in Sweden and Denmark. The very same phenomena, as I hope I shall indicate, are seen in the erratic-blocks of Hemelum. Besides Silurian formations, others, both older and younger, are numerous represented. At the same time all of them show almost exclusively a West-baltic character.

We should then see the remarkable phenomenon that at Groningen, which is situated between Kloosterholt and Rijs, erratic-blocks greatly differ from those of the two places mentioned.

Gradually, however, I am beginning to doubt whether my opinion about the character of the erratic-blocks in the Groningen Hondsrug should be the right one. In the years when I used to gather there, digging was almost entirely confined to the upper layers, so the chances are, that deeper parts contain other kinds of erratic-blocks.

A few facts seem to indicate this. First of all: while a deep cave was being dug under the brewery called Barbarossa, at Helpman, big blocks of Saltholmlime with *Terebratula lens* Nilss made their

¹⁾ VAN CAALKER, Ueber eine Sammlung von Geschieben von Kloosterholt. Zeitschr. d. Deutsch. Geol. Gesellsch. Jahrgang 1898 p. 234.

BONNEMA, De sedimentaire zwerfblokken van Kloosterholt. Versl. v. d. Koninkl. Akad. van Wetensch. te Amsterdam 1898 pag. 448.

appearance. Some pieces of this material are still to be seen in the Geological Institute at Groningen.

Secondly: VAN CALKER¹⁾, — when the ramparts near one of the gates (Boteringepoort), which ramparts had certainly been made of the boulder-clay from the very deep ditches in that neighbourhood, were dug off, — found some erratic-blocks consisting of kinds of stone such as I never found afterward, and which do not occur in the Russian Baltic-Sea provinces, i.e. slate with graptolites, Faxe-lime and sandy glauconite lime-stone with *Terebratula lens* Nilss.

Deeper cuts made into the Hondsrug may afterwards give us an opportunity of learning whether my original opinion was entirely right, or is the true one only as far as the outer layers are concerned.

I should now like to tell something about the chief Cambrian pieces that are found in my collection. I am going to treat only of those stones whose age may be more or less precisely determined.

I. Lower-Cambrian Stones.

1. *Scolithus*-sandstone. Eleven stones consisting of this material are found in my collection. Nine of them are typical grey, quartziferous *Scolithus*-sandstone, showing a peculiar, fatty lustre on the side where they were broken off. No layers are visible as long as the stone is not changed by the influence of the weather. Only if this takes place, the layers become more or less visible. In one stone they are rather distinct and turn upward (perhaps downward) near the "*scolithus*." Two other stones, one of which is blue-grey, whilst the other moreover contains red parts, are clearly divided into layers and contain much finer tubes than are found in the typical stone. In the regions from which our erratic-blocks come, *Scolithus*-sandstone was first seen as firm rock in the isle of Runö near Oscarshamm, where according to TORELL²⁾ it was discovered by Dr. HOLMSTRÖM. Afterwards it was also met with as such by NATHORST³⁾, in the isle of Furön, not far from Runö.

I was wrong when, in treating of the Kloosterholt erratic-blocks, I told that *Scolithus*-sandstone as firm rock is found in Sweden, in the neighbourhood of Lund and Kalmar. The same mistake was

¹⁾ VAN CALKER, Beiträge zur Kenntniss des Groninger Diluviums. Zeitsch. d. deutsch. geol. Gesellsch. Jahrg. 1884 pag. 718 and 727.

²⁾ TORELL, Petrificata Suecana formationis cambricae. Lunds Univ. Årsskrift, Tom. VI 1869 pag. 12.

³⁾ NATHORST, Geol. Föreningens i Stockholm Föreläsningar 1879. Bd IV, pag. 293.

made by SCHROEDER VAN DER KOLK ¹⁾ and by STEUSLOFF ²⁾. The latter and I probably came to make it under the influence of what was told by ROEMER ³⁾ with regard to the origin of this kind of erratic-blocks. With SCHROEDER v. D. KOLK this is certainly the case, as appears from the note at the bottom of the page.

As to their being found at Hardeberga in the neighbourhood of Lund, ROEMER seems to have forgotten the fact that TORELL ⁴⁾, though he at first communicated that the Hardeberga sandstone contained worm-shaped bodies probably belonging to *Scolithuslinearis* Hall, afterwards makes mention of a new kind, viz. *Scolithuserrans* TORELL ⁵⁾. The latter are distinguished for being mostly curved and running through the stone in various directions.

ROEMER's information that TORELL describes *Scolithuslinearis* from an erratic-block found near Lund, and that according to NILSSON *Scolithus*-sandstone occurs near Calmar (as firm rock), must be attributed to an error. If my imperfect acquaintance with the Swedish language does not deceive me, TORELL ⁶⁾ writes that the place where the pictured stone (an erratic-block) was found, cannot be indicated for sure, but that NILSSON thinks he remembers that it was found near Calmar.

In the Northern part of the Netherlands erratic-blocks of *Scolithus*-sandstone are rather common. In Frisia were found, besides the stone treated of above, one in the Roode klif (Red Cliff) ⁷⁾, one in the Mirnsercliff ⁸⁾ and one at Warns (see number 3). Among the erratic-blocks of the Gron. Hondsrug ⁹⁾ only one piece was found up to this time, whereas I formerly described already two pieces from Kloosterholt ¹⁰⁾ and afterwards gathered more of them there. In the

1) SCHROEDER VAN DER KOLK, Bijdrage tot de kennis der verspreiding onzer kristallijne zwervelingen. Dissertatie pag. 50.

2) STEUSLOFF, Sedimentärgeschiebe von Neubrandenburg. Archiv des Vereins der Freunde der Naturgeschichte in Mecklenburg. Jahrg. 45 pag. 162.

3) ROEMER, Lethaea erratica pag. 23.

4) TORELL, Bidrag till Sparagmitetagens geognosi och paleontologi. Lunds Univ. Årsskrift. Tom. IV. pag. 35.

5) TORELL, Petrif. Succ. format. cambric. pag. 12.

6) TORELL, Bidrag till Sparagmitetagens geogn. och paleontol. pag. 29.

7) VAN CAPPELLE, Bijdrage tot de kennis van Frieslands bodem. II pag. 12.

8) VAN CAPPELLE, Les Escarpements du „Gaasterland”, pag. 236.

9) VAN CALKER, Ueber das Vorkommen cambrischer und untersilurischer Geschiebe bei Groningen. Zeitschr. d. deutsch. geol. Gesellsch. Bd XLIII pag. 793.

10) VAN CALKER, Ueber eine Sammlung von Geschieben von Kloosterholt, pag. 235. BONNEMA, De sedim. zwerfblokken van Kloosterholt, pag. 449.

province of Drente VAN CALKER¹⁾ mentions Buinen, Steenberg and Zeegse as places where he came across these stones, whereas I myself found some at Odoorn.

2. Grey sandstone with interlaced coloured layers.

A small piece of quartziferous sandstone, 7 centimetres long, is almost entirely grey-coloured. Two systems of coloured layers, varying from red to violet, interlacing under angles of about 30 degrees, are also found. The layers of each system separately run parallel to each other. Surfaces of deposit do not occur and the size of the grains of sand is everywhere the same, so that it is impossible to examine which layer-system runs parallel to them.

This sandstone was made mention of for the first time by NATHORST²⁾, who found erratic-blocks consisting of it in Jungfrun in the Kalmarsund. With DAMES³⁾ he found the same kind of stone in Oeland, a few years after. Later on the latter writer⁴⁾ could tell about this kind of erratic-block occurring in diluvial layers in the neighbourhood of Berlin.

As one of the pieces found there contains Scolithus-tubes, he could also draw the conclusion that their age is the same as that of the above mentioned Scolithus-sandstone. This conclusion is confirmed by means of a piece of Scolithus-sandstone that I found at Warns a short time ago. Through the grey piece of sandstone run on one side a few violet-coloured layers, which are intersecting the Scolithus-tubes under an angle of 60 degrees, while the latter always stand perpendicularly on the surfaces of deposit, which are not seen here.

That this stone also occurs in the Dutch diluvium, was already shown by VAN CALKER⁵⁾; he proves that it is found in the erratic-blocks of the Gron. Hondsrug.

II. *Mid-Cambrian Stones.*

3. Limesandstone with Paradoxides-remains.

In my collection I have also a piece of grey, fine-grained sandstone with a large quantity of calcium-carbonate as binding-material.

¹⁾ VAN CALKER, Ueber ein Vorkommen von Kantengeschieben und von Hyolithus- und Scolithus-Sandstein in Holland. Zeitschr. d. deutsch. geol. Gesellsch. Jahrg. 1890 pag. 583.

²⁾ NATHORST, Geol. Föreningens i Stockholm Förhandlingar 1879. Bd IV pag. 293.

³⁾ DAMES, Geol. Reisenotizen aus Schweden. Zeitschrift der deutsch. geol. Gesellschaft. Jahrg. 1881 pag. 417.

⁴⁾ DAMES, Zeitschr. d. deutsch. geol. Gesellsch. Jahrg. 1890. Bd XLIII pag. 777.

⁵⁾ VAN CALKER, Zeitschr. der deutsch. geol. Gesellsch. Jahrg. 1891. Bd XLIII pag. 793.

Through the stone run intersecting passages of the same mineral. Here and there are small grains of glauconite and pyrites-crystals. Besides many Paradoxides-fragments arranged in layers, my stone contains remains of horn-shelled Brachiopoda. The former are cream-coloured and do not allow of being further defined. Among the latter are easily found valves of *Acrotele granulata* Linn.

About this stone I have up to this time nowhere found any information. It is probably of the same age with the layers of *Paradoxides Tessini* Brongn., or it is a little older than these are.

4. Gravel-stone with *Paradoxides Tessini* Brongn.

a. It is a piece of fine-grained, hard sand-stone, yellow-grey inside and light grey nearer the surface, whilst the surface itself is brown in some places. With a magnifying-glass some grains of glauconite and a few mica-scales may be distinguished in it.

With muriatic acid applied to it, there is no effervescence; consequently it does not contain calcium-carbonate. There are no layers.

The chief remnant occurring in this erratic-block is a mid-shell, a little more than 1 centimetre long, of a *Paradoxides*, which mid-shell is visible for the greater part. The cream-coloured shell is still almost entirely present. That this remnant originates from *Paradoxides Tessini* Brongn., could be easily determined by means of the description and the pictures which LINNARSSON ¹⁾ gave us of this kind. Prof. MOBERG, to whom I had the honour of showing this erratic-block, when visiting Lund, thought my determination right.

The glabella increases in breadth towards the front; quite near the front it is broadest. The front-edge is rounded off. On each side the glabella has two side-furrows, which in the middle run into those of the other side, which is also the case with *Paradoxides Oelandicus*. Of smaller furrows, which according to LINNARSSON are sometimes found in the latter, nothing is to be seen here. The edge before the glabella is very narrow in the middle and broadens towards the ends. This is characteristic of *Paradoxides Tessini*, whilst with *Paradoxides Oelandicus* the breadth of the edge before the glabella is rather considerable, and remains about the same towards the sides.

We also find here a piece of a thorax-ring of a kind of *Paradoxides*, in which it may be seen that the pleurae first run straightway towards the outside and then turn to the back, forming an almost right angle. This also occurs with *Paradoxides Tessini*, whereas with *Paradoxides Oelandicus* this turning to the back takes place gradually.

¹⁾ LINNARSSON, Om Faunan i Kalken med *Conocoryphe exulans* („*Coronatus kalken*”). Sveriges geologiska undersökning. Series C. N^o 35 pag. 6. Scene I fig 1—4.

Finally are found in this erratic-block a few small valves of horn-shelled Brachiopoda, among which is one of *Lingula* or *Lingulella*.

b. Besides the piece treated of just now I found a piece of sandstone with *Paradoxides*-remains, which shows no effervescence when hydrochloric acid is applied to it, and which consequently is gravel-stone.

It is a flat piece, consisting of two parts of a different nature. One of them is formed by sandstone and does not present many layers. This sandstone greatly resembles the material of which consists the erratic-block treated of under *a*, but is a little bluish. Some small mica-scales and glauconite-grains are also present here. The other part shows many more layers and has a dark bluish-grey colour. Sometimes the layers are as thin as paper, so that the material becomes slate-like.

Just as in the other piece of stone, the *Paradoxides*-remains are cream-coloured here. They are, however, too fragmentary to enable us to draw the conclusion that they originate from *Paradoxides Tessini*. As up to this time, however, only sandstone with this kind of *Paradoxides* has been found in diluvial grounds, and the petrographical nature of one part of them bears a great resemblance to that of the previous piece, I think I may suppose this much, and I venture to range this erratic-block under this head.

I think that both pieces originate from a layer-complex of gravel-stone with *Paradoxides Tessini*-remains, which complex consisted both of slate-like blue-grey parts and of thicker light-coloured layers. The last-mentioned erratic-block may originate from the former, whereas the one treated of under *a* would be a piece of a thicker layer.

If my supposition is not false, it may be easily explained from the difference in firmness and the difference in fitness for being transported issuing from this, why in literature nothing is found about erratic-blocks that should bear resemblance to the last-mentioned piece, whilst two or three communications have been received about the finding of erratic-blocks that most probably are more like the piece treated of in the first place.

The first communication we got from ROEMER.¹⁾ It deals with a piece of gravel-stone that was found in a sand-pit of Nieder-Kunzendorf near Freiberg in Silesia. It seems to have been more exposed to the influence of the weather than the erratic-block found by me, the writer mentioned speaking of a ferruginous outer crust, while round my piece such a crust begins to form itself.

Probably I must also range among this kind a piece of sandstone

¹⁾ ROEMER, Zeitschr. der deutsch. geol. Gesellschaft. Bd 9. Jahrg. 1857 pag. 511.

with Paradoxides Tessini-remains that was found in the collection of Groningen erratic-blocks, given to the geological Institute at Lund by Mr. DE SITTER, L. L. D., then burgomaster of Groningen. It was described by LUNDGREN¹⁾. I am sorry that we do not learn whether it is gravel-stone or lime-sandstone. I wrote to Prof. MOBERG, director of the Institute mentioned above, in order to ask after this, but he could not give me any information concerning the piece just then. I think, however, that it is gravel-stone, LUNDGREN telling us that the colour is „gråhvit“, while according to ROEMER²⁾ lime-sandstone with Paradoxides Tessini is dark grey.

While in the previous case it has not yet been with certainty determined which kind of sandstone one has to deal with, REMELÉ³⁾ has announced another gravel-stone with Paradoxides-remains having been found. This erratic-block differs from the piece I described under *a* in the fossils being coloured brown by manganite-superoxide. However, I think this of little importance, as it may be just as well a consequence of infiltration that occurred in diluvial grounds or even before that time.

Gravel-stone with Paradoxides Tessini has up to this time not been met with as firm rock. Probably it occurs as such, or did so in former times, in the neighbourhood of Oeland; for on the Western coast of this isle is found, in several places, lime-sandstone with the same kind of trilobites.

III. Upper-Cambrian Stones.

5. Alum-slate with *Agnostus pisiformis* L. var. *socialis* Tullb.

One time I was so fortunate as to find a piece of black slate, in which are scattered the grey head- and tailshields, preserved in relief, of a kind of *Agnostus*. They have a length and a breadth of 3 millimetres at most.

The head-shields are moderately vaulted. The dorsal furrows meet in front, and a tongue-shaped glabella is bounded by them. At the front-part of the glabella is on each side a lateral furrow. The two lateral furrows run into each other and in this way cut off a small part in front. At the foot of the glabella two small lobes are separated from the rest by means of two lateral furrows slanting backward. The central, largest part of the glabella shows

¹⁾ LUNDGREN, Geologiska Föreningens i Stockholm Förhandlingar. 1874. II N^o 2 pag. 44.

²⁾ ROEMER, *Lethaea erratica*, pag. 29.

³⁾ REMELÉ, *Zeitschr. der deutsch. geol. Gesellschaft*. Bd 35. Jahrg. 1883 pag. 871.

in the midst a wedge-shaped elevation. The cheeks are in front separated by a furrow running from the front of the glabella to the edge-furrow.

The tail-shields are much more vaulted. This is especially the case with the rhachis, which broadens towards the back and stretches nearly as far as the edge. Consequently, the lateral parts of the pygidium, which are already narrow, become even more so towards the back part. They are not separated by a furrow, as it is the case with those of the head-shields. The pygidia have at the back-edge on either side a little cog pointing backward. The rhachis of the pygidia is clearly divided into three parts. The back-part is the largest by far and is particularly swollen. The lateral furrows of one side do not meet those of the other, as they are separated by a wedge-shaped elevation passing on from the second part to the first and ending towards the back in a blunt point slanting upward.

From the properties mentioned it may be easily seen why this kind of *Agnostus* was described by TULLBERG¹⁾ as *Agnostus pisiformis* L. var. *socialis*. Pictures of it have been given by BRÖGGER²⁾ and POMPECKI³⁾.

Up to this time this erratic-block is the only piece of alum-slate with *Agnostus pisiformis* L. var. *socialis* that was found in our diluvial grounds. In Germany they also seem to be very rare. Only GOTTSCHÉ⁴⁾ mentions such a piece from SCHULAU. This one also contains, however, remains of *Olenus truncatus* Brömm. As firm rock such alum-slate with this variety of trilobites occurs in Sweden (Oeland and Bornholm included), in different places, as I learned from Prof. MOBERG, to whom I showed a piece of the erratic-block.

Microbiology. — *"Accumulation experiments with denitrifying bacteria"*. By G. VAN ITERSON JR. (Communicated by Prof. M. W. BEJERINCK).

The great signification of the denitrifying bacteria for the circulation of nitrogen in organic life and the important biochemisms to which they give rise, made the study of these organisms very attractive.

1) TULLBERG, Om *Agnostus*-arterna i de Kambriska aflagringarne vid Andrarum. Sveriges geologiska Undersökning. Ser. C. N^o 42 pag. 25.

2) BRÖGGER, Die Silurischen Etagen 2 und 3 im Kristianiagebiet und auf Eker. Pag. 56. Taf. 1. fig. 10 a b c.

3) POMPECKI, Die Trilobiten-Fauna der Ost- und Westpreussischen Diluvialgeschiebe. Beiträge zur Naturkunde Preussens herausgegeben von der Physikalisch-Oekonomischen Gesellschaft zu Königsberg. Pag. 15, Taf. IV, fig. 24 a b.

4) GOTTSCHÉ, Die Sedimentär-Geschiebe der Provinz Schleswig-Holstein, pag. 11.

In the first place it was necessary to subject their distribution in nature and their isolation to an investigation, because the literature thereon offers but very deficient data. The best way to attain this object seemed to try whether the method of "accumulation" gave in this case, as in so many others, any definite result, and that for the following reasons.

The character of this way of experimenting is the cause, that many biological properties of the species there by accumulated may be predicted;

it renders it possible, in a simple way, directly and with certainty to isolate from nature a determined species; this is of special interest inasmuch the cultures of most bacteria, by being kept in the laboratoria, change their character to such a degree as to become irreconisable, so, that the descriptions, found in bacteriological literature, according as they are made after newly isolated or long kept material, may be wholly different;

it teaches us to recognise the sought- for species in the different varieties occurring in the material used for infection, as these varieties are bound to corresponding culture conditions;

the identification and synonymy of the bacteria, which are always extremely difficult, even in case we possess good descriptions, made of freshly isolated cultures, are much facilitated by good "accumulation experiments";

these may, moreover, be controlled by anyone, and render the investigator independent from material isolated by others.

For the arrangement of my experiments I have followed the example given by Dr. H. H. GRAN ¹⁾ of Bergen in his researches in the Bacteriological Laboratory at Delft on denitrifying sea bacteria.

By exclusively using nitrate as source of nitrogen in the culture liquid, which was contained in a cotton-plugged flask, so that the air could freely enter, he succeeded to restrict considerably the number of developing species of bacteria, when taking fresh sea-water for infection, bringing the denitrifying species to vigorous growth. He furthermore selected, as source of carbon the calciumsalts of organic acids, by which the prejudicial alkaline reaction, which appears in bouillon in consequence of the decomposition of the alkalinitrate, was avoided. Mostly calciummalate was used, which is a very good bacterial food, and has moreover the advantage of solving only to 0,8 % at 25° C., so that it can be added to an excess, whence, as the salt is oxidised, a new quantity is solved.

¹⁾ Studien über Meeresbacteriën I, Bergens Museums Aarbog 1901 N^o. 10.

After 2 or 3 successive inoculations in the same liquid a constant bacterial mixture was obtained.

I tried to apply these principles to the isolation of denitrifying land-bacteria, and so-doing I succeeded indeed, when using calcium-tartrate as source of carbon, to accumulate *Bacillus vulpinus*, hereafter to be discussed.

It proved however to be a fundamental improvement wholly or partly to exclude the access of air as thereby the growth of the denitrifying bacteria is not in the least impeded, whilst a number of other aerobic bacteria are very much hindered in their development.

Of the numerous methods of culture under exclusion of air I have followed the simplest, namely the "bottle method", long since in use in the Bacteriological Laboratory at Delft for the examination of the sulphate reduction by microbes and the lactic-acid fermentation. For my experiments this method proved perfectly adapted, as the quantity of air which finds access, can thereby easily be regulated. An ordinary, narrow-mouthed stoppered bottle, with an exactly fitting stop, is quite or partly filled with the culture liquid, and after sterilising or not, according to circumstances, the bottle is placed in the thermostat for culture.

1. *Historical.*

The reduction of nitrates by bacteria constantly begins with the formation of nitrite. This may be further converted in five different ways, viz. :

1st. It may be reduced to ammonia.

2nd. It may be converted into unknown, nonvolatile nitrogen compounds.

3rd. If in the liquid acid is formed simultaneously, it may give rise to the development of nitrogen-oxygen compounds.

4th. It may be decomposed in alkaline solution under formation of nitrogen-oxygen compounds.

5th. The nitrite may, in alkaline solutions, give rise to the development of nitrogen without the production of nitrogen-oxygen compounds. This is *denitrification proper*, of which here is only question.

Already in 1814 DAVY¹⁾ states that during putrefaction of animal matter nitrogen as such is freed. "Here it is again seen," says in 1860 G. J. MULDER²⁾, from whom I borrow this particular, "if one wishes

1) Elemente der Agriculturchemie, Berlin 1814, S. 309.

2) De Scheikunde der Bouwbare Aarde, 1860, dl. 3, blz. 58.

truly to give the enique suum in this part of science, one often must retrograde half a century."

Not before 1856 the problem was again taken into research. In that year REISET¹⁾ pointed out, that at the putrefaction of dung and flesh free nitrogen is produced. Later investigators have not been able to observe free nitrogen under these circumstances, inasmuch as no nitrate or nitrite are present, but the putrefaction of albuminous matter as such has still remained an open question from this point of view.

It was PELOUZE²⁾, who in 1857, for the first time, with certainty stated the disappearance of nitrate during the putrefaction of animal matter.

BOUSSINGAULT³⁾ observed in 1858 the disappearance of salt-peter in the soil. He ascribed it "à une cause purement accidentelle, à une action reductrice, exercée par de la matière végétale morte".

From the year 1873 date very interesting observations of SCHLOESING⁴⁾ on nitrification. By studying the influence of oxygen on this process, he was led to the examination of denitrification. He found that nitrification in the soil was still very active, when it was held in a current of gas, which contained but 1,5 % oxygen. If he worked in a current of pure nitrogen, there not only occurred no nitrification, but even the nitrate, originally in the soil, disappeared entirely. He furthermore proved that at this decomposition nitrogen is formed.

Experiments of PASTEUR and the well known investigation of SCHLOESING and MÜNZ on nitrification, induced GAYON and DUPETIT⁵⁾ to ascribe denitrification to the action of micro-organisms. In 1882 they communicated their first results and these put the bacterial nature of the process out of all doubt. Their elaborate and excellent researches on this subject were published in 1886⁶⁾.

Our compatriots GILTAY and ABERSON⁷⁾ isolated, for the first time, in 1892 a denitrifying ferment, and the prescription given by them for the artificial culture liquid has been followed by various later investigators.

The attention of bacteriologists was again fixed on these ferments

1) Expériences sur la putréfaction et sur la formation des fumiers. C. R. 1856, T. 42, p. 53.

2) Remarques de M. PELOUZE. C. R. 1857, T. 44, p. 119.

3) Nouvelles observations sur le développement des *hélianthus* soumis à l'action du salpêtre donné comme engrais C.R. 1858, T. 47, p. 807.

4) Etude sur la nitrification dans les sols, C.R. 1873, T. 77, p. 203.

5) Sur la fermentation des nitrates, C.R. 1882, T. 95, p. 644.

6) Recherches sur la réduction des nitrates par les infiniments petits. Nancy. 1886.

7) Recherches sur un mode de dénitrification et sur le schizomycète qui la produit. Arch. Neerl. T. 25, 1892, p. 341.

by interesting agricultural experiments of P. WAGNER ¹⁾ in 1895, which seemed to point out a danger produced by these bacteria for agriculture.

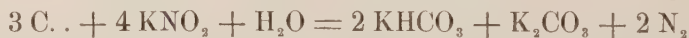
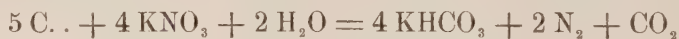
His experiments gave direct cause to the research of BURRI and STUTZER ²⁾, who, in the same year, elaborately described two denitrifying bacteria.

From that time this group has been laboriously studied and at present a number of twenty denitrifying species have been described ³⁾.

To these I for my own part might add some ten species more, but of these I will only discuss those, for which I can point out an accumulation experiment, which gives a constant result.

2. General considerations.

The hitherto isolated denitrifying bacteria are all aerobic. In liquids containing nitrate or nitrite, they can, however, grow vigorously with a very slight or without access of air, so that in this case they behave like anaerobic bacteria. They then transfer the oxygen of the nitrate or the nitrite to the organic compounds present in the culture liquid. Thence nitrogen is freed and the metals of the salts pass into carbonates or bi-carbonates, which process may be represented by the formulae:



The correctness of this representation has been proved by the observations of GAYON and DUPETIT, GILTAY and ABERSON, PFEIFFER and LEMMERMANN, AMPOLA and ULIANI, and also by my own researches.

We see from this, that in a liquid, simultaneously with the nitrate, the rate of organic substances decreases, and accordingly also the permanganate number. From a practical point of view this must necessarily be of signification for the explanation of the processes on which is based the biological purification of sewage and water ⁴⁾.

My experiments have furthermore convinced me that denitrification is inseparably connected with the growth, for which traces of free oxygen are always necessary.

¹⁾ Die geringe Ausnützung des Stallmiststickstoffs und ihre Ursachen, Landw. Presse, 1895, S. 92.

²⁾ Ueber denitrifizierende Bakterien. Centrbl. f. Bakt. Abt. II, Bd. 1, 1895, S. 257.

³⁾ O. LEMMERMANN. Kritische Studien über Denitrifikationsvorgänge. Jena. 1900. G. HÖFLICH. Vergleichende Untersuchungen über die Denitrifikationsbakt. etc. Centrbl. f. Bakt., Abt. II, Bd. 7, 1902, S. 245.

⁴⁾ Dr. JENNY WEYERMAN. Biologische stelsels tot reiniging van rioolvocht, enz. Vragen des Tijds. Febr. 1901, Sep., blz. 38.

In 1897 WEISSENBERG ¹⁾ pronounced the hypothesis, that, at the reduction of nitrate to free nitrogen, nitrite constantly appears as interphase. I can perfectly well share this view, and that for the following reasons:

1st. All denitrifying species which I have studied in the course of this research could, in as much as they produced free nitrogen from nitrate, do the same from nitrite.

2nd. Like BURRI and STUTZER (l.c.) I have been able to isolate a species, which does convert nitrite into free nitrogen, but leaves nitrate intact, so that from a mixture of nitrite with a little nitrate, all the nitrite is removed by this bacterium, whilst the nitrate remains unchanged.

Here I must however observe, that at the conversion of nitrate into free nitrogen, not always nitrite can be detected in the culture. This fact has already been stated by SEWERIN ²⁾ and KÜNNEMANN ³⁾. It is however by no means in contradiction with WEISSENBERG's hypothesis, for if the course of the second process: decomposition of nitrite, is quicker, or as quick as the first: reduction of nitrate, the nitrite-phase is no more to be demonstrated.

KÜNNEMANN observed this fact in a variety of *B. stutzeri*, which observation I have been able to confirm; however, in my opinion, the cultural conditions played in this experiment a much more important part than the character of the variety. In bouillon with 0,1 % KNO_3 , I could often point out no nitrite, whilst here a strong development of gas took place. On the other hand, I obtained with 4 and 5 % KNO_3 only a slight gas development, but a strong reaction of nitrite.

For the investigation of a colony on its denitrifying power, sterile test-tubes were filled with 10 à 15 Ccm. of bouillon, as well with 0,1 % KNO_3 as with 0,1 % KNO_2 and then inoculated. Denitrifying bacteria grow therein sufficiently, after 24 hours to produce a distinct turbidity, whilst, at the surface they form a scum-layer. Sometimes the scum is wanting, but is produced at shaking the test-tube.

Besides were used solutions of calcium-salts of organic acids, decocts of pease-leaves with 2 % cane-sugar, and decocts of potatoes, likewise with 0,1 % KNO_3 or KNO_2 .

In this case a control experiment was made to decide, whether without addition of nitrate or nitrite, these solutions might cause

1) Studien über Denitrification. Arch. f. Hygiene. 1897, Bd. 30, S. 274.

2) Zur Frage über die Zersetzung von Salpetersauren Salzen durch Bakterien. Centrbl. f. Bakt. Abt. II, 1897, Bd. 3, S. 504.

3) Ueber denitrifizierende Mikro-organismen. Landw. Versuchs-Stat. 1898, Bd. 50, S. 65.

development of gas, which proved never to be the case with denitrifying bacteria.

In order to obtain perfectly convincing results, to the said culture liquids 10 % gelatin often was added and, when in the boiled solution, at about 30° C., some of the culture had been suspended, it was poured into a test-tube and solidified. The developing gas then remains as bubbles, nearly at the place of its origin, in the gelatin. This method ("tube-culture") produces a sharp reaction on denitrification, especially when controlled by a parallel experiment, using the same culture gelatin, without nitrate or nitrite.

This principle may also be used for a rough computation of the number of denitrifying germs in any material. So it was proved that circa 2000 of these organisms occur in 1 gr. of garden soil, and circa 100 in 1 gr. of canal water.

In these experiments the potassium-salts may be replaced by sodium- or magnesium-salts; calcium-nitrate, on the other hand, prevents even in dilute solution the growth of many bacteria.

Before passing to the description of the different accumulation experiments, I have to make a general remark about their arrangement.

Which species finally becomes most common in the used culture liquid depends on many circumstances, difficult to control, in particular on the mutual numerical proportion of the individuals and the nature of the different species in the material originally used for the infection, and likewise on the condition of the microbes themselves in consequence of previous circumstances.

This explains why, when using different materials of infection for the accumulation of one and the same species, it is sometimes necessary to modify the cultural conditions in accordance with the nature of that material.

I insist on this circumstance in particular to explain the different accumulation experiments described under *B. stutzeri*, on the one hand from water by using tartrate, on the other hand from soil by using malate.

3. *Accumulation of Bacterium stutzeri*, LEHMANN and NEUMANN¹⁾.

This interesting bacterium was isolated in 1895 from straw by BURRI and STUTZER (l.c.), whilst in 1892 BRÉAL²⁾ had already shown the presence of denitrifying bacteria thereon.

¹⁾ LEHMANN u. NEUMANN. Bakteriologie. München 1896, S. 237.

²⁾ De la présence dans la paille d'un ferment aérobie, réducteur des nitrates. C.R. 1892, T. 114, p. 681.

In 1898 KÜNNEMANN (l.c.) isolated the same species from soil and a variety from horse-dung and straw.

By accumulation experiments, logically carried out, I have succeeded in obtaining this bacillus from soil, canalwater, sewage-water and horse-dung.

The following experiment always led practically to a pure culture from canalwater:

A bottle of about 200 Ccm. is partly filled with fresh canalwater with addition of 2% calcium-tartrate, 2% KNO_3 and 0,05% K_2HPO_4 ¹⁾, computed after the whole capacity. Then the bottle is filled up to the neck with canalwater and the stop is loosely put in, so that a little water is pressed from the bottle. In this way it is filled without a single bubble of air and, after shaking, put in a thermostat of 25° of 28°. The calcium-tartrate solves at this temperature for only 1%, so that this salt remains for a great part at the bottom.

Commonly already after one day a feeble production of gas is to be observed, issuing from the non-solved calcium-tartrate at this bottom. The process gets into full course after three or four, sometimes only after five days. So much gas thereby is produced that a coarse, slimy scum originates at the surface and a great quantity of the liquid is pressed out of the bottle. The gas containing only nitrogen and carbondioxyd, the culture remains anaerobic. The liquid grows turbid by the growth of the bacteria and the fine, cristalline calcium-tartrate changes into coarsely granular calcium-carbonate. After a week, in consequence of the scum formation, the bottle is nearly half void, and after about 12 days the reaction is at an end, in as much, corresponding with the chosen quantity of tartrate, all nitrate has disappeared.

If a vigorously growing culture is sown on broth gelatin, a mixture is obtained of colonies of various different species, from which *B. stutzeri* can easily be isolated, if we are once acquainted with it.

From such a bottle some drops are inoculated into a bottle of about 50 ccm. capacity ¹⁾, which, after sterilisation, is filled for $\frac{3}{4}$ with the following sterile culture liquid:

Tap-water, 2% calcium-tartrate, 2% KNO_3 and 0,05% K_2HPO_4 .

After inoculation the bottle is quite filled up with the same liquid in the above described way, and after the lapse of two or three days, the same phenomena appear as in the first bottle.

If now, once more, of this transport a plate culture on broth gelatin is made, the great diminution in the number of species is

¹⁾ The capacity of the bottle is not indifferent.

surprising. All liquefying colonies, and most fluorescents have disappeared, whereas, among two common and some less frequently occurring species, *B. stutzeri* develops in great numbers and is easily recognised by the characteristic properties of its colonies.

By repeating the said transport this bacterium may still be more multiplied, so that, after three or four successive inoculations, practically a pure culture of this species is obtained.

From soil of the garden of the Bacteriological Laboratory I regularly obtained the same bacterium, in the course of the winter of 1901—2 by applying the "bottle method" with this liquid:

Tap-water, 2 % calcium-malate, 1 % KNO_3 and 0,05 % K_2HPO_4 .

In the spring, however, though there were constantly some colonies of the species, the number of its germs proved so small that they were replaced by other denitrifying bacteria, particularly *B. denitrofluorescens*, of which more presently.

A detailed description of *B. stutzeri* is given by BURRI and STETZER (l. c.), as well as KÜNNEMANN (l. c.). It will therefore be sufficient here to give the chief characteristics by which this species is directly recognised.

The bacterium is a short, thick rodlet with a peculiar vibrio-like motion.

The colonies on gelatin are extremely characteristic (see Plate). After three or four days they have a diameter of about 0.5 mm. and after a week they attain 1 to 1.5 mm. When magnified they then resemble a rosette, or have an irregularly folded or crispate, greyish surface. The peculiar structure appears only distinctly, when the glass-dish which contains the plate culture, is reversed and the colony is seen through the bottom with about a 30-fold magnification. The most frequent shapes are represented in figures 1—4.

But it may happen that the crispate character becomes still more conspicuous and then the image is as in fig. 5.

Commonly it seems as if regularly arranged smaller colonies are situated in the larger ones, which may often be observed till in the outer border, and points to a peculiar periodicity of the mucus secretion in the interior of the colony.

In the colonies moreover a fine deposit is observed, and sometimes very distinct crystals, which may also be found in the gelatin around.

All these characteristics are particularly marked when the cultures have been recently isolated, but they may in the course of time get lost or become indistinct. Another property however remains always quite distinct, i.e. the adhering to the gelatin. Young colonies can only be removed in one piece, and of the older always part remains behind.



Fig. 1.

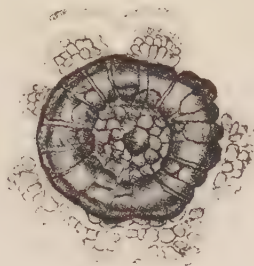


Fig. 2.



Fig. 3.

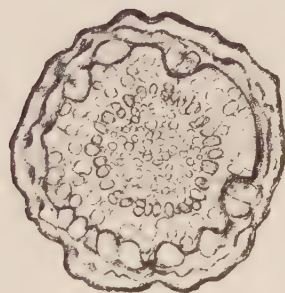


Fig. 4.

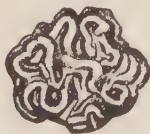


Fig. 5.

Very characteristic also is the growth of this bacterium on a sterilised slice of potato, where the curled and folded structure of the colonies is quite distinct, in consequence of the large dimensions they attain. The colour changes thereby into flesh-red. Old cultures grow soft in consequence of a dissolving process the slimy substance.

The compounds which can provide the carbon and nitrogen nutrition of this species were determined by means of the auxanographic method ¹⁾, this giving in a simple way a measure for the difference in assimilability of the nutritive substances.

With KNO_3 as source of nitrogen, a feeble growth was observed with glucose and maltose. Kalium-succinate, malate, malonate, citrate and calcium-tartrate, gave rise to a vigorous growth. No growth was obtained with cane sugar, milk sugar, mannite, galactose and oxalic acid.

The auxanograms prove that tartrate belongs to the best assimilable substances, which explains why its use in the accumulation experiment with canal water produces such good results.

With kalium-citrate as source of carbon, NH_4Cl , KNO_3 , KNO_2 , asparagin, kalium-asparaginate and pepton, could serve as source of nitrogen.

B. stutzeri produces no invertin, does not split indican and ureum but it secretes diastase, although in very slight quantity. This latter fact explains the possibility of denitrifying by this species in solutions containing, besides the salts, only amylum and KNO_3 . In broth no indol and no sulphureted hydrogen are produced.

B. stutzeri produces much alkali; even the presence of glucose does not prevent the production of it in a plate of broth gelatin.

Very remarkable is the behaviour of *B. stutzeri* towards free oxygen.

If the arrangement of the moving individuals under the influence of the oxygen of the air ²⁾ is examined in the glassroom, we find an accumulation in a line at rather great distance from the meniscus. On the other hand, growth is only observed ³⁾ in the meniscus itself. Hence, in this respect the bacterium behaves quite in accordance with the aerobic spirilla.

B. stutzeri is a very active denitrifying species; to broth could be added up to 4% KNO_3 , and up to 1% KNO_2 , without thereby preventing the development of gas. If in the before described way a "tube

¹⁾ BEYERINCK. L'auxanographie ou la méthode de l'hydrodiffusion dans la gélatine appliquée aux recherches microbiologiques. Arch. Neerl. 1889, T. 23 p. 367.

²⁾ ENGELMANN, Zur Biologie der Schizomyceten. Botanische Zeitung 1882, Bd. 40, S. 320.

³⁾ BEIJERINCK, Ueber Atmungsfiguren beweglicher Bakteriën. Centr.bl. f. Bakt. 1893, Bd. 14, S. 827.

culture" in broth gelatin is made, with 0,1% KNO_3 , after two or three days the gas bubbles will appear over the whole length of the tube, and herein this species differs from *B. vulpinus*, where the gas bubbles originate at some distance from the meniscus only.

I will finally make mention of an instructive experiment I performed with *B. stutzeri*. Some garden soil was mixed with tapwater with 0,05 % K_2HPO_4 , and a thin layer of this mixture in an ERLÉNMEYER-flask exposed to a temperature of 25° C. Under these circumstances the production of nitrate becomes very marked after two weeks. If now the whole content of the ERLÉNMEYER flask is poured into a stoppered bottle, which thereby is quite filled, whilst *B. stutzeri*, is used for infection, soon a development of gas sets in and the nitrate disappears completely. Hence it follows that according as the air enters our culture liquid well or not, nitrification or denitrification may occur. This is quite in accordance with older experiences described by SCHLOESING (l. c.) in regard to the soil in general.

4. *Accumulation of Bacillus denitrofluorescens n. sp.*

SEWERIN (l. c.) found in 1897 that *B. pyocyaneus* belongs to the denitrifying ferments. But the group of fluorescents proper was long fruitlessly examined as to their denitrifying power, first by LEHMANN and NEUMANN and afterwards by WEISSENBERG (l. c.). In 1898 KÜNNEMANN isolated for the first time a denitrifying bacterium, which liquefied gelatin and fluoresced.

Though in my experiments I often obtained fine cultures of a similar species, I did not succeed in finding a satisfactory accumulation experiment for it. On the other hand I found such an experiment for a non-liquefying fluorescent *Bacillus*, which I named *B. denitrofluorescens*.

The culture liquid for the accumulation of this species is:

Tap-water, 2 % calcium-citrate, 1 % KNO_3 and 0,05 % K_2HPO_4 .

In a bottle of 50 Ccm. capacity, 1 to 2 gr. fresh garden soil is put; it is then quite filled up with the culture liquid, in the way described under *B. stutzeri*. The culture is made at 25° C.

When sowing on broth gelatin the 2nd or 3rd transport, successively kept in the same culture medium, I always obtained cultures containing almost exclusively colonies of that species.

In horse-dung, canal water and sewage water, I also observed this bacterium, but it is with more certainty to be isolated from soil.

In exterior appearance of the colony this species differs in no respect from one of the most common fluorescents, characterised by

lacking, on the culture gelatin, the smoothly spreading border. In young broth gelatin cultures, the pigment fluoresces blue, and after some time a white precipitate forms in the gelatin.

Examined auxanographically, KNO_3 as source of nitrogen proved to cause a feeble growth with mannite, a vigorous one with kalium-malate, citrate, malonate, succinate and tartrate, as well as with glucose and levulose. On the other hand no growth is seen with cane-sugar maltose, milk-sugar, and raffinose.

In broth, with 2 % glucose, this bacterium, like all fluorescents, produces acid. Broth with 2 % cane-sugar, becomes however strongly alkaline, which is observed also in all other fluorescent secreting no invertin.

This bacterium neither produces diastase, nor can it hydrolise indican or ureum. In broth it forms no sulphureted hydrogen and no indol.

In its behaviour towards free oxygen it likewise corresponds with the fluorescents, i.e. with the cover-glass culture in the humid room, both motion and growth cause accumulation in the meniscus.

This makes the bacterium strongly contrast with *B. stutzeri* and *B. vulpinus*, whose motion figures show the spirillum type.

As to the energy of its denitrifying power *B. denitrofluorescens* corresponds with *B. stutzeri*. At the "tube experiment" with broth gelatin with 0.1 % KNO_3 , the bubbles form over the whole length of the tube, quite in the same way as with *B. stutzeri*.

5. Accumulation of *Bacillus vulpinus* n. sp.

Already in my introductory observations I remarked, that an accumulation experiment with full access of air, when using tartrate and nitrate, produced this species, but the accumulation obtained in this way was still very imperfect. By cultivating under *partly* exclusion of air, I succeeded in improving the experiment very much. I obtained this result by enclosing in the culture bottle with the liquid a determined volume of air, and reinoculating from bottle to bottle under the same conditions three or more times. It is true that thereby not all other species are totally removed, but this is no obstacle to the recognition of *B. vulpinus*, whose colonies are extremely characteristic, possessing a quite unique brown-red pigment.

The experiment is as follows:

Into a bottle of 50 Ccm. 1 to 2 grams of fresh garden soil is put, and further it is filled up with the following culture liquid, whilst leaving on air bubble of 2 Ccm: Tap-water, 2 % Calcium-tartrate, 0.1 % KNO_3 , and 0.05 % K_2HPO_4 .

Here likewise the culture is effected at 25°.

With observation of the said proportion and operating as described under *B. stutzeri*, the different varieties of *B. vulpinus* can also be obtained from canal water.

The denitrification sets in very slowly and the development of gas gets not by far the intensity perceived in the preceding species. Here, too, by the complete disappearance of all liquefying bacteria already at the first transport, the isolation of the wished for species is much facilitated. Although at sowing the crude cultures on broth gelatin some *B. vulpinus* colonies may already be perceived, they multiply so much in the transports, that plates therewith prepared, appear, so to say, quite covered with the large, flatly spread, transparent, fox-coloured colonies of this species.

If for the accumulation other organic salts than tartrate are used, or a higher rate of nitrate than 0.2 %, not a single colony of *B. vulpinus* is detected, though it was certainly present in the infection material as it is universally, distributed in the soil.

By their growth the colonies strongly remind of the flatly spread variety of *B. fluorescens non liquefaciens*, but of fluorescence nothing is seen. In shape and motility the bacterium corresponds with *B. stutzeri*.

An interesting property of *B. vulpinus* is, that the brown pigment only develops under the influence of light. If simultaneously two cultures of this species are made on broth gelatin, and one, wrapped in black paper, is put in the dark, and the other in the light, for the rest in equal conditions, a great difference is perceptible. This becomes more obvious still, when making reinoculations or transports of either culture, likewise keeping these respectively in the dark and the light. So-doing a perfectly colourless culture can be obtained, but if this is again inoculated in the light, the brown colour returns. The pigment formation only takes place at growth, so that colonies, full-grown in the dark do not colour when exposed to light.

B. vulpinus belongs to the group of real chromophores¹⁾, i. e. the pigment is bound to the bacterial body, and the behaviour towards light is, in my opinion, another indication that in this group the pigment has a biological function.

The auxanographic examination proved, that with nitrate for nitrogen nutrition, a feeble growth is obtained with kalium-malonate, a vigorous one with levulose, glucose, maltose, kalium-citrate, succinate

¹⁾ See BEIJERINCK, La biologie d'une bactérie pigmentaire. Arch. Néerl. 1892, T. 25, p. 227.

acetate and tartrate, whereas cane-sugar, milk-sugar, mannite and raffinose produce no growth at all. Ammonium-chloride may also serve as source of nitrogen, when using tartrate for carbon nutrition.

Pepton, asparagin, and kalium-asparaginate may simultaneously serve as C and N-nutriments.

The bacterium secretes neither invertin nor diastase and does not split indican or ureum. In broth it produces no sulphureted hydrogen but a little indol.

In the "tube experiment" in broth gelatin with 0,1 % KNO_3 , bubbles of nitrogen are exclusively seen to form at a little distance from the meniscus, and moreover, the culture of this species not succeeding in a bottle *wholly* filled with a culture liquid containing nitrate, we must needs conclude, that *B. vulpinus* wants considerable quantities of oxygen for the denitrification.

As regards the other species, which form gas bubbles also in the depth of the tube, I have come to the conviction that they too, want traces of free oxygen to this end.

Notwithstanding this different behaviour towards free oxygen, the motion figure, like that of *B. stutzeri*, shows the spirillum type.

By modifying the nutrient liquids and temperatures I have succeeded, as observed above, in accumulating various other denitrifying bacteria, beside those described. Thus I obtained, at 37° C. with calcium-citrate and 0,2 % KNO_3 , under exclusion of air, and using garden soil for material of infection, the spirillum-like *B. indigofærus* VOGES¹⁾, which denitrifies only feebly, but is interesting by its indigo-like pigment. When using sewage water, I obtained a strongly denitrifying, liquefying, blue pigment bacterium, not yet described.

Of all these experiments however, the result is not constant enough to be inserted here.

6. Summary and conclusions.

1st. The fundamental principle of my accumulation experiments was partly or completely to prevent the access of air. By this means I have succeeded, by cultivating in solutions of organic salts and nitrate, only by repeated transports in the same liquid, in bringing many denitrifying bacteria to a more or less perfectly pure culture.

¹⁾ CLAESSEN. Ueber einen indigoblauen Farbstoff erzeugenden Bacillus aus Wasser. Centrbl. f. Bakt. 1890, Bd. 7, S. 13.

VOGES. Ueber einige im Wasser vorkommende Pigmentbacteriën, Centrbl. f. Bakt. 1893, Bd. 14, S. 301.

Of these experiments three always gave constant results, and produced respectively *B. stutzeri* NEUMANN and LEHMANN, *B. denitrofluorescens* n. sp. and *B. vulpinus* n. sp.

2nd. *B. stutzeri* deserves attention on account of the unique structure of its colonies, as seen in Fig. 1—5 on our Plate.

3rd. *B. denitrofluorescens* is the first example of a denitrifying, non liquefying fluorescent.

4th. *B. vulpinus* is a chromophorous pigment bacterium, whose pigment only forms at growth in the light.

5th. *B. stutzeri* and *B. vulpinus* behave towards free oxygen like aerobic spirilla, *B. denitrofluorescens* behaves like an ordinary aerobic bacterium.

6th. Like in soil and dung, in which it had also been found by other experimentators, I have established the general distribution of denitrifying bacteria in canal and sewage water.

7th. The denitrifying bacteria can, even with the slightest quantities of various organic substances, cause the disappearance of determined quantities of nitrate under development of free nitrogen.

8th. In one and the same culture medium, where nitrification is produced during aeration, denitrification may be caused by exclusion of air, this holds good also in regard to the soil.

At the end of this paper I want to express my sincere thanks to Professor Dr. M. W. BEIJERINCK for his kind, invaluable guidance and efficacious assistance, afforded me in these researches.

Delft, July 1902.

Physics. — "*An Hypothesis on the Nature of Solar Prominences.*"

By Prof. W. H. JULIUS.

The introduction of the principle of anomalous dispersion into solar physics makes it possible to form an idea of the Sun's constitution from which necessarily follow i.a. a great many peculiarities of prominences, which, until now, it has been impossible to deduct in a satisfactory manner from other physical laws. This I will show in the following pages.

In my paper on "*Solar Phenomena, etc.*" read Febr. 24, 1900. I put forth the following hypothesis with respect to that part of the solar atmosphere, situated outside what is called the photosphere¹⁾:

¹⁾ W. H. JULIUS, *Solar Phenomena*, considered in connection with Anomalous Dispersion of Light, Proc. Roy. Acad. Amsterdam, II, p. 585.

"The various elements, whose presence in that atmosphere has been inferred from spectral observations, are much more largely diffused in it than has generally been assumed from the shape of the light phenomena; they may be present everywhere, up to great distances outside the photosphere, and yet be visible in few places only; their proper radiation contributes relatively little to their visibility (with perhaps a few exceptions); the distances, at which the characteristic light of those substances is thought to be seen beyond the Sun's limb, are mainly determined by their local differences of density and their power to call forth anomalous dispersion."

How we were to imagine the condition of the matter inside the photosphere, was not considered there. Our hypothesis on the origin of the light of the chromosphere was kept free from any special conceptions as to the nature of the photosphere. Only where the principle of anomalous dispersion was made use of also to explain spectral phenomena observed in sunspots ¹⁾, we had to fall back upon A. SCHMIDT's theory ²⁾, according to which the Sun is an unlimited gasball, so that the apparent surface of the photosphere should not be considered to be the real boundary of a body, but to correspond to a "critical sphere", defined by the property that its radius equals the radius of curvature of horizontal rays, passing through a point of its surface.

At present, however, in working out the problem of the nature of the chromosphere and the prominences, we likewise will take as a starting point the first of the three Theses, in which SCHMIDT sums up the main points of his theory. Accordingly, we suppose the Sun to be an unlimited mass of gas, in which the density and luminosity (not considering local irregularities) gradually diminish from the centre outward. But our conception of the properties and composition of this gaseous body can in a certain respect be much simpler than would be the case, if we accepted the whole of SCHMIDT's theory.

Indeed, SCHMIDT explains both the edge of the Sun's disk by the laws of regular refraction (or ray-curving) in a stratified medium, and the prominences by refraction in "Schlieren" ³⁾; but in order to account for the fact that the light from the prominences as well as that from the chromosphere, instead of being white, shows a bright line spectrum of varying appearance, he supposes the strongly radiat-

¹⁾ l. c. p. 585.

²⁾ A. SCHMIDT, Die Strahlenbrechung auf der Sonne. Ein geometrischer Beitrag zur Sonnenphysik. Stuttgart 1891.

³⁾ A. SCHMIDT, Erklärung der Sonnenprotuberanzen als Wirkungen der Refraction in einer hochverdünnten Atmosphäre der Sonne. SIRIUS XXIII S. 97—109, Mai 1895.

ing mass of gases in its outer parts to be composed so as to emit almost exclusively hydrogen-, calcium-, heliumlight, whilst the radiations of sodium, magnesium, titanium, iron are supposed to originate in deeper layers, a.s.o. ¹⁾. We, on the contrary, by the introduction of anomalous dispersion are permitted to suggest, that throughout the gaseous body, as well inside as outside the critical sphere, the various elements are altogether intrinsically mixed (granting that in the mixture the quantity of materials with greater specific gravity must grow with the depth). For wherever there are local differences of density in the mixture, caused by currents, whirls etc., the conditions for irregular ray-curving are present, and it is evident that specially those elements of the mixture, which possess an exceptionnally high dispersing power for certain waves of the transmitted light, will be able to reveal their presence even at great distances from the disk, while other substances, though also present at the same places, remain invisible there. Thus a purely optical explanation may be given of the fact, that the different gases of the sun are *seen* separated, even though we suppose them to *be* thoroughly mixed.

And surely this last supposition is the simpler by far; it even necessarily follows from the fundamental idea, that the Sun may be considered as a rotating, heat-radiating mass of gas, for in such a body the constituent parts must continually mix.

A few months ago the main character of the motion that must go on in a sun, supposed to be gaseous, has been discussed by R. EMDEN ²⁾. He applies to the Sun the same mathematical deductions, which had been devised by VON HELMHOLTZ for investigating the kind of motion which in our terrestrial atmosphere must result from the united influence of heating by the Sun and of the daily rotation ³⁾. Though EMDEN supposes the gaseous Sun to be limited by a well-defined surface, and so far accepts the prevailing views on the constitution of this celestial body, still his mathematical formulae are absolutely independent of the existence of a boundary surface, and so are fully applicable to a sun, such as we are considering here.

Radiation causes the outer layers to cool down soonest; they sink inwards and are replaced by ascending hotter gases, so that,

¹⁾ As appears from a paper in the Physik. Zeitschr. 3. S. 259—261: entitled „Ueber die Doppellinien im Spectrum der Chromophäre" SCHMIDT adheres to this conception, even after having taken into consideration the possibility of explaining the light of the chromosphere by anomalous dispersion.

²⁾ R. EMDEN, Beiträge zur Sonnentheorie. Ann. d. Phys. [4] 7, p. 176—197.

³⁾ H. VON HELMHOLTZ, Gesammelte Abhandlungen I, p. 146, III p. 287—355.

if the Sun did not rotate, we could only expect radial convection currents. But the rotation of the sun completely changes this form of motion; the angular velocity of descending masses increases, of ascending masses diminishes; there will be found side by side gas-layers of different densities, and rotating at different speeds.

It has been shown by VON HELMHOLTZ, that during a certain time such gaslayers can flow side by side, sharply separated by a so-called surface of discontinuity (i. e. by a surface, on passing which the values of the velocity and the density change with a leap); but gradually the friction causes this surface to undulate; the waves advance with the more swiftly moving layer, they grow steeper, overhang and break, forming whirls; and thus, by the mingling of the adjacent parts of the two layers a new layer is formed between them, the properties of which will be intermediate between the corresponding properties of the original layers.

From the conditions of the problem we may deduce the position of the surfaces of discontinuity. This has been performed by von HELMHOLTZ with regard to the air-currents in our atmosphere, and by EMDEN for the rotating layers of the Sun. He arrives at the conclusion, that in the Sun the surfaces of discontinuity must in the main have the shape, figured in the accompanying sketch and reminding us of hyperboloids of revolution ¹⁾.

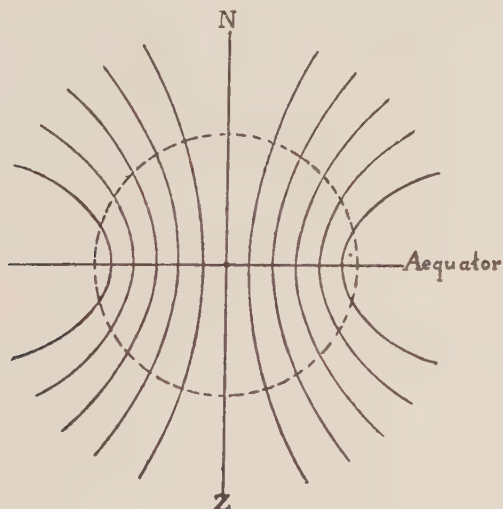


Fig. 1.

¹⁾ EMDEN draws the intersections of the surfaces with the plane of the paper only inside the circle, representing the sun's boundary. I have dotted this circle, with a view to indicate, that the border is only a seeming one; accordingly I prolonged the intersections outward.

In every annular layer, bounded by two consecutive surfaces of discontinuity, the moment of rotation of unit mass ($\Omega = \omega r^2$) as well as the so-called potential temperature θ are constant; but in a following layer, farther from the Sun's axis, Ω has a greater and θ a smaller value. Within every layer there exists a velocity potential, but at the separating surfaces the linear velocity changes discontinuously, the difference between the velocities on each side of one and the same separating surface increasing as that surface approaches the axis.

The waves, that are formed in the separating surfaces, will proceed in the direction of the rotation, and when, after growing steeper and steeper, they break, the resulting vortices will have their core-lines perpendicular to the direction of motion of the waves, i.e. coinciding with the generatrices of the surfaces of discontinuity. So, the curves in our figure also give an idea of the position of the vortex-cores.

From the theory follows, as we already mentioned, that at each definite surface of discontinuity the leap of the velocity is greater at a short than at a long distance from the Sun's axis; therefore, the transition from a wave into a whirl must, as a rule, begin in those parts of that wave, which are nearer to the axis, and appear afterwards in the outer parts.

Further it is clear that, because every whirling leads to mingling of the adjacent parts of two layers and to the formation of two new surfaces of discontinuity, there will never exist a complete surface, such as indicated by our sketch. Everywhere we shall meet with pieces of surfaces of discontinuity; only their main character and the average direction of the vortex-cores will correspond to the sketch. And in spite of the continual mixing of layers, which leads to equalization of differing rotational velocities, the motion still remains nearly stationary; for within each layer, temporarily enclosed between two surfaces of discontinuity, the convection currents carry cooled matter inwards and hot matter outwards, by which process the differences in rotational velocity are renewed.

Forced as we are to admit, that such an uninterrupted mixing process is going on in the Sun, the advantage of explaining the chromosphere and the prominences by anomalous dispersion of white light, must appear to us very obvious. All other explanations, that I know of, must start from the hardly tenable supposition, that the different gases of the chromosphere are separately present in large quantities.

EMDEN has succeeded in deducing many properties of sun-spots from the supposition, that the spots show us the places, where huge whirls attain the Sun's surface. It seems to me that EMDEN's views

on sun-spots would become even much more acceptable, if the notion of a real surface of the Sun were given up and if the consequences of normal and anomalous refraction (better ray-curving) in those whirls were allowed for. But to this subject I desire to come back on another occasion.

For the present we will confine our attention to those parts of the whirls, optically projecting beyond the edge of the Sun's disk, and we propose the hypothesis, that the whole chromosphere with all its prominences is nothing but this system of waves and whirls, made visible within shorter or longer distances from the Sun's edge by anomalous dispersion of light, coming from deeper layers.

(Perhaps the structure of the corona, with its polar streamers, arches, etc., might tell us something about the course of the surfaces of discontinuity at very great distances outside the critical sphere; this point too, however, I will only hint at here).

So we ascribe the chromosphere to the smaller vortices, to the continual rolling up of the surfaces of discontinuity; in the prominences we see the whirling, in which the rarer, very large waves of the solar ocean dissipate.

The particular structure of the chromosphere, suggesting the comparison with a grass-field in vertical section, follows immediately from this hypothesis. Prominences likewise nearly always show a tissue of stripes, bands and filaments¹⁾. These, according to our view, indicate the position of the whirl-cores. In the whole region, where whirling is going on, the density will, of course, vary in a very irregular way; we therefore may expect to find in the spectrum of that region as well the light on the red as that on the violet side of the absorption lines, i. e. the chromospheric and flash lines must be double lines²⁾.

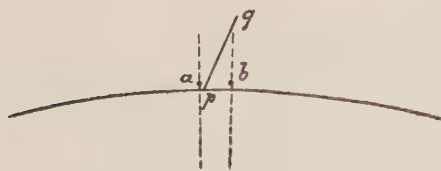


Fig. 2.

the light, coming from *b*. Indeed, following in *a* the Sun's radius

Along the core of a vortex the density is a minimum. If, now, a vortex intersect the apparent limb of the sun obliquely, as in Fig. 2, where *pq* represents the core-line, the light coming from a point *a* must differ from

¹⁾ J. FÉNYI S. J., *Protuberanzen*, beobachtet in den Jahren 1888, 1889 und 1890 am Haynald—Observatorium, p. 5. (Kalocsa, 1902).

²⁾ W. H. JULIUS, On the Origin of Double Lines in the Spectrum of the Chromosphere, Due to Anomalous Dispersion of the Light from the Photosphere. *Proc. Roy. Acad. Amst.* Vol. III, p. 193.

outward, we at first get into layers of increasing density, whereas, ascending from *b*, we meet with layers of decreasing density. Consequently, in the spectrum of *a* the "violet-facing" components of the double lines must be prominent and in the spectrum of *b* the red-facing ones. If the slit be placed tangentially, through the points *a* and *b*, the two cases will be seen at a short distance on the same spectral lines. And when during a total eclipse of the Sun the chromospheric arc itself functions as a slit (the prismatic camera being used), the same phenomenon may be met with on numerous places of the crescents. Many instances thereof are visible on the plates, obtained in Sumatra by the Dutch expedition for observing the total eclipse of May 18th 1901.

With large prominences the phenomenon sometimes appears very intensely. In the important work by FÉNYI, mentioned before, we read for instance on p. 121, in the description of a carefully observed prominence, the following passage:

.... „Im unteren Teile zeigte die Protuberanz am Anfange ihrer Entwicklung eine grosse Störung in der H_{α} Linie. Bei engem (tangentiell gestelltem) Spalte reichten zwei Spitzkegel über denselben hinaus, der eine, grössere erstreckte sich gegen rot, der andere kleine gegen blau und stand etwas südlicher. Die Grösse des ersteren betrug 9" im Gesichtsfelde; auf Grund einer neuen Bestimmung der thatsächlichen Dispersion des Spektroskops ergibt sich daraus für diese Stelle der Protuberanz eine Bewegung *von* uns mit der Geschwindigkeit von 240,4 Klm. in der Secunde. Die Verschiebung gegen blau betrug nach dem Augenmaasse etwa die Hälfte der ersteren gegen rot.

Die entgegengesetzten Bewegungen neben einander und die Kegelförmige Form des veränderten Lichtes würden unschwer die Deutung auf eine Wirbelbewegung am Grunde der Protuberanz gestatten. Aus der Ungleichheit der Kegel würde ein Vorschreiten des Wirbels *von* uns mit der Geschwindigkeit von 180 Klm. sich ergeben. Die Beobachtung steht auch nicht allein da; eine ähnliche Erscheinung wurde von YOUNG am 3. Aug. 1872 (*The Sun*, p. 210) eine andere von THOLLON in Nizza (*C. R.* XC p. 87, XCI p. 487) beobachtet; ähnliches wurde auch von mir bei anderen Gelegenheiten beobachtet."

Thus, interpreting the light on both sides of the hydrogen-line after DOPPLER's principle, FÉNYI arrives at the very astonishing conclusion, that the whirling mass of hydrogen moves at a speed of 180 kilometers per second. Moreover, there is a much greater difficulty, not even mentioned by FÉNYI, viz. that the coherent outbuds of the line impose upon him the necessity of supposing that velocity to be very different for the various parts of the whirl, adjacent

pieces of the prominence not even taking any part in the enormous motion along the line of sight.

The above-given explanation of the phenomenon by anomalous dispersion solves all these mysteries.

It occurs very seldom that prominences show a rapid sideward motion, i.e. a motion in the meridian of the Sun. FÉNYI mentions as an exceptional case a sideward velocity of 25 kilometers per sec¹). As, on the other hand, velocities of 250 kilometers and more in the direction of the parallel (calculated after DOPPLER) are by no means a great exception, we meet with contradictions — as is admitted also by FÉNYI — from which it appears impossible to escape, unless we doubt the reality of the velocities.

It is surprising and satisfactory to see how nearly all the peculiarities in the behaviour of prominences, as described by YOUNG, FÉNYI and many others, appear quite intelligible as soon as we look at these phenomena from our point of view.

Let us choose only a few more examples out of the vast material.

FÉNYI says (l. c. p. 115): „Schon seit Jahren habe ich bemerkt, dass helle hervortretende Punkte in der Chromosphäre, welche eine kleine Verschiebung gegen blau zeigen, der Ort sind, wo alsogleich der Aufstieg einer Flamme oder einer kleinen Protuberanz erfolgt.“

Now the process of whirl-formation in a surface of discontinuity proceeds, as a rule, from the inner parts of the Sun outwards. In the axis of a whirl the density is a minimum. Consequently, at the moment the whirling reaches the apparent edge of the Sun, a minimum of density will be found just projecting beyond the edge. Here we have a place, where the density increases from the photosphere outward and where, therefore, the violet-facing component of the chromospheric double-line temporarily prevails: it seems as if a shifting towards the violet occurs. Shortly afterwards the more distant parts set a whirling and the prominence appears.

In the description of a great prominence, observed by FÉNYI on the 18th of Aug. 1890, we read i.a. the following particulars²):

„Ein ganz besonderes Interesse verleihen dieser an und für sich schon grossartigen Erscheinung die Eigenbewegungen in der Gesichtslinie, die an derselben beobachtet wurden. Eine ungefähr zwischen 40" und 50" Höhe liegende Schicht, (deren Lage in der beigegebenen Figur genau bezeichnet ist), zeigte eine heftige Bewegung gegen die Erde zu. Das rote Licht des Hydrogeniums ergoss sich daselbst in verworrenen Formen über den Spaltrand gegen blau hinaus ohne

¹) FÉNYI, l. c. p. 114.

²) FÉNYI, l. c. p. 129.

indessen den Spalt ganz zu verlassen. Die Bewegung war durchaus local, die Umgebung zeigte keine Spur einer Bewegung. Die Geschwindigkeit derselben war keine ungewöhnlich grosse; ich erhielt aus 4 mit dem Fadennikrometer gemachten Messungen zwischen 11 h. 45 m. und 12 h. 15 m. verschiedene, zwischen 94 und 201 klm. schwankende Werthe. Was aber die Erscheinung zu einer besonders merkwürdigen gestaltet ist der Umstand dass, während diese in der Höhe vor sich gehende ganz locale Bewegung nicht einer Ausströmung zugeschrieben werden kann, dieselbe trotzdem doch eine halbe Stunde lang beobachtet wurde! Nehmen wir als Mittelwerth der Geschwindigkeit 150 klm. per Secunde an, so hätte dieser bewegte Teil der Protuberanz während der zwischenzeit von 30 Minuten gegen 270.000 klm. durchlaufen, also wohl auch den scheinbaren Ort ändern müssen."

Of course this contradiction immediately vanishes if we only suppose, that in the part of the prominence, showing the persistent shift of the hydrogen light towards the blue, the density of the solar matter was increasing in the direction from the photosphere outwards. This supposition is quite in harmony, too, with the fact, that the picture of this prominence shows very important whirling *below* the part in question and no disturbance worth mentioning *above* it.

Observers have often been puzzled at the rapid disappearing of enormous prominences and at the perfect calm in the whole region, including the Sun's surface, a short time after such a violent "eruption" had taken place. It was hardly conceivable that the ejected incandescent gases could loose their huge quantities of heat so rapidly, nor that the eruption had no further visible consequences.

In our theory a large prominence is nothing but the visible token, that whirling is going on almost simultaneously over vast regions. The very important varieties of density in the whirling mass may, however, be annulled by displacements of much matter over relatively small distances, which process, of course, may go on without violent movements and yet be accomplished in a short time. So there is no reason whatever to expect, that a great prominence will leave the medium in a highly disturbed condition.

Whosoever wishes to consider prominences as eruptions, must grant, that it is one of the most difficult problems to account both for the tremendous values of the ascending velocities sometimes observed and for the most capricious way, in which the speed often suddenly changes without any conceivable cause. The 20th of Sept. 1893 FÉNYI witnessed a prominence ascending 500000 kilometers in a quarter of an hour, that is at an *average* velocity of more than

550 kilom. per sec. In another case, also observed by FÉNYI (July 15th 1889), in the course of 10 minutes the ascending velocity passed through the values 72, 6, 65, 24, 154 kilometers per second; and with the prominence of Oct. 6th, 1890, in 30 minutes' time through the values 33,8, 79,8, 67,6, 72,7, 127,7 275,5, 242,3, 121, 57,3 kilom. per sec.

Considering the problem from the new point of view we see the difficulties disappear in consequence of the observation, that, properly speaking, we have not to do with velocities at all. We may speak of the velocity with which matter moves or with which a disturbance is transmitted by a medium; but neither of these cases is met with here. Wherever the whirling sets in, it results from local conditions and cannot be considered as directly transmitted from places, where whirling was going on a little earlier. Though it is true that, as a rule, the breaking of a wave begins in those parts of a surface of discontinuity, that are nearer to the Sun's axis, and from there proceeds outwards, yet this does not involve that we should have a right to call this process a transmission of matter or of motion in the direction of the vortex-cores. And where there is no transmission, there is no velocity.

When at the sea-shore a wide wave approaches and breaks, now here, then farther and farther, nobody will speak of the „velocity” with which the foam or the whirling is moving along the coast. Every body knows, that the foam, the visible token of the whirling, is successively formed at different places. Such about is the case with the prominences, the visible spots in the breakers of the solar ocean.

Chemistry. — Professor LOBRY DE BRUYN communicates a paper by himself and Mr. J. W. DITO. *“The boilingpoint-curve of the system: hydrazine + water”*.

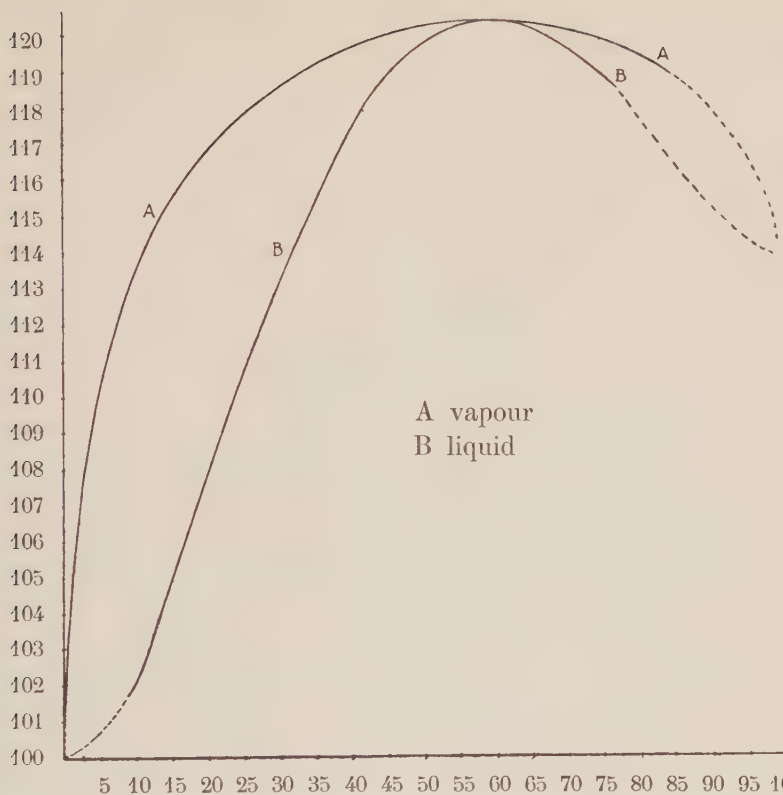
In a previous report¹⁾ Mr. DITO has communicated the results of determinations of the densities of mixtures of hydrazine and water; the figures showed that a maximum density corresponds exactly (or nearly so) with the composition $N_2H_4 \cdot H_2O$. At the end of that note it was stated that we would endeavour to determine the boilingpoint-curve of the system: hydrazine + water.

We have lately been engaged with that determination; the result is given in the following table and annexed curve.

¹⁾ Proc. of April 19, 1902, p. 838.

Amount of mixture and barometer.	Temp.	Number mols. of N_2H_4 on 100 mols.	
		liquid.	vapour.
	102.2	9.4	0.18
300 grm. 755.5 ↓	104.6	14.2	
"	105.9		1.6
"	107.45	19.5	2.7
"	109.15		3.9
"	111.0		6.2
"	114.95	34.0	13.8
"	117.95	41.7	25.0
85 gr. 768.0	118.6	42.9	30.3
"	119.2	45.2	34.9
"	119.8	50.3	41.7
38 gr. 770.8	120.2	51.8	44.6
"	120.35	53.3	48.75
"	120.45	54.8	52.8
"	120.5	56.0	53.5
	[120°5	58.5	58.5]
771.1	120.45	62.5	
"	120.25	65.8	72
"	119.9	68.3	75.5
"	119.5	72.7	81
"	119.25	73.6	83.7
50 gr. " ↑	118.8	76	

It should be observed beforehand that the figures obtained, particularly those relating to the mixtures rich in hydrazine, cannot possess that accuracy attainable with other mixtures. In the first place free hydrazine is a costly substance; working with a large quantity such as is required for the accurate determination of a boilingpoint curve, therefore, leads to not inconsiderable expenses. Moreover, free hydrazine and its mixtures with little water (also the hydrate $N_2H_4 \cdot H_2O$) are very hygroscopic and also easily oxidisable by the oxygen of the air. During the volumetric determination of the amount of



hydrazine in the liquid and condensed vapour, it was impossible to avoid contact with the atmosphere. The operation was carried out in such a manner that each time after distilling off a certain quantity (10—20 c.c. in the case of the greater concentrations), two portions (3—4 drops) of the condensed vapour and residue were simultaneously collected in tared weighing bottles containing about 5 c.c. of water. On account of the many weighings a certain time necessarily elapsed between the taking of the samples and the titration and, considering that the bottles also contained a little vapour of hydrazine mixed with air, this must have exercised some influence. This explains why the agreement between the various duplicate determinations often left much to be desired; in one case a discrepancy occurred amounting to 2 mols. per 100. Finally, another source of error is found in the fact that on account of the many weighings and titrations, the determinations had to be done on different days, so that the distillations were conducted under different barometric conditions.

Notwithstanding this, the results allow of the construction of a curve, the regular course of which is a guarantee that the figures observed

express the entire phenomenon with a certain amount of accuracy. As already stated, more correct results can only be obtained by repeating the experiments with larger quantities of hydrazine ¹⁾.

Our experiments have led to the interesting result that hydrazine-hydrate does not at all represent a chemical compound $N_2H_4 \cdot H_2O$ with a constant boilingpoint of about 120° , as hitherto believed. This however is not surprising, particularly after KNIETSCH's experiments on the system sulphurtrioxide + water ²⁾. The tendency of SO_3 and H_2O to enter into combination is greater than that of N_2H_4 and H_2O . As the boilingpoint curve of the system sulphurtrioxide + water shows a maximum not belonging to the compound H_2SO_4 but to a mixture of 98,5 % of H_2SO_4 and 1,5 % of H_2O , it is not at all surprising that in the system hydrazine + water the maximum does not correspond with the composition $N_2H_4 \cdot H_2O$. It is seen from these figures that a liquid boiling at $119^\circ.8$ and having the composition 50 mols. N_2H_4 + 50 mols. of H_2O yields a vapour containing about 42 mols. of N_2H_4 and 58 mols. of water, while a vapour of about the composition $N_2H_4 \cdot H_2O$ is given off at $120^\circ.4$ by a liquid containing about 54 mols. of N_2H_4 and 46 mols. of water.

From the course of the curve it appears that a maximum boilingpoint of about $120^\circ.5$ corresponds with a liquid with about 58 mols. of N_2H_4 . The experiment has shown that a mixture of about 58.5 mols. of N_2H_4 and 41.5 mols. of H_2O has a constant boilingpoint of $120^\circ.1$ at 760 m.m. In the table $120^\circ.5$ therefore corresponds with 771 m.m.

The course of the first half of the curve plainly shows the phenomenon observed by CURTIUS namely, that on boiling dilute solutions of hydrazine the distillate consists at first almost exclusively of water, although the boilingpoint has very sensibly increased. It may be assumed that the same thing happens in the reverse case of much hydrazine and little water; for reasons stated we have not been able to ascertain this.

One of us (DITO) is already engaged with the determination of the viscosity of the system: hydrazine + water; while with the co-operation of Professor ERNST COHEN experiments have already been started, several months ago, on the electrolytic conductivity of the same system and of solutions of salts in hydrazine ³⁾.

¹⁾ Ber. **34**, 4088 (1901).

²⁾ CURTIUS states that concentrated solutions of hydrazine attack glass when boiling at ordinary pressure. We did not notice any such action of even highly concentrated solutions on our glass fractional distilling apparatus and condensing tube.

³⁾ Recueil **15**, 179.

Chemistry. — Professor LOBRY DE BRUYN presents, also in the name of Mr. W. ALBERDA VAN EKENSTEIN, a communication on "*Formaldehyd (methylen-) derivatives of sugars and glucosides.*"

In a previous communication ¹⁾ we have already stated that an aqueous solution of formaldehyde when evaporated with some of the sugars reacts on the same. This was shown by the great changes in the rotation. We then also remarked that attempts to isolate the crystalline compounds from the syrupy mass had not proved successful. These, moreover, are readily dissociated by evaporation in the presence of much water, the pure sugars being left behind. ²⁾

About the same time ³⁾ TOLLENS had prepared a crystallised methyleneglucose by mixing a solution of glucose in formaldehyde with hydrochloric and acetic acids and setting the liquid aside for some months. He obtained a monoformal-derivative which still powerfully reduced FEHLING's liquid. Other sugars gave a negative result.

On continuing our researches it appeared that substances, of an apparently different nature and more stable than those occurring in the said syrups, are formed when the dry sugars are melted with polymerised formaldehyde (trioxymethylene). The rotatory power then appears strongly modified and the reducing power decreased: this, however, reaches its normal figure on boiling with dilute acid. From this follows that during the reaction of the sugar with the formaldehyde, the aldehyde groups disappear.

We now succeeded in isolating in the case of several sugars (and glucosides) crystallised compounds or such having a constant boiling point, by introducing the fused mass into sulphuric acid of various concentrations or phosphoric acid and then agitating the liquid with an organic solvent such as chloroform, which dissolves the diformal compounds. In some cases there are formed, simultaneously, monoformal derivatives which are readily soluble in alcohol and water, but sparingly soluble in chloroform and so behave in this respect quite the reverse from the diformal derivatives.

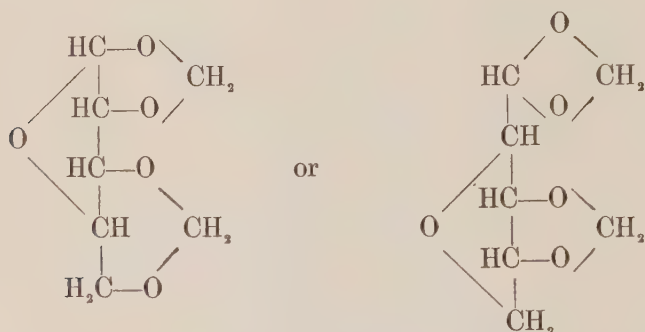
Both the di- and the mono-methylenesugars no longer react with FEHLING's solution and behave indifferently toward phenylhydrazine; the carbonyl groups have therefore disappeared during the action of the formaldehyde. After boiling with dilute acids, the reducing power returns. These substances must therefore in the first place

¹⁾ Proc. 1900. 9.

²⁾ RUFF and OLLENDORFF, Ber. **32**. 3236 (1899), have regenerated some sugars from different hydrazines by evaporation with solution of formaldehyde.

³⁾ Ber **32**. 2585 (1900); his experiments had commenced some years previously.

be regarded as glucosides, derived from methyleneglycol $\text{CH}_2(\text{OH})_2$ ¹⁾, which is unknown in the free state. Two of the alcoholic hydroxyl groups of the sugar-molecule have also taken part in the formation of the diformal-derivatives. A hydroxyl group is no longer present in formalmethylenexyloside and -arabinoxide, for acetic anhydride and benzoyl chloride do not act on these substances. As, according to the analysis, two mols. of water have been eliminated, the following constitutional formulae, for instance, may be drawn up for the said pentose derivatives.



Diformalxylose ($\text{C}_7 \text{H}_{10} \text{O}_5$) crystallises very neatly from benzene or light petroleum; melting point $56^\circ\text{--}57^\circ$, $[\alpha]_D$ (2% solution in methylalcohol) $= +25.7$; may be readily sublimed.

Diformalarabinoxide is a somewhat oily, colorless liquid which may be distilled in vacuum without decomposition. Boiling point 155° at about 32 m.m. pressure; $[\alpha]_D$ (2% solution in methylalcohol) $= -16^\circ$.

With glucose a syrupy diformalderivative may be separated from a solid mono-compound by taking advantage of the said difference in solubility. Neither of these substances have any reducing power or react with phenylhydrazine. They are probably mixtures; the white substance, although crystalline, does not possess a definite melting point ($140\text{--}150^\circ$) and on analysis gives no satisfactory figures, but it could not up to the present be resolved by recrystallisation into components. The diformal-derivative, left in contact with solvents for many months, remained syrupy.

Both compounds still contain one or more free hydroxyl groups ;

¹⁾ The methyleneglucose obtained by TOLLENS (l.c.) has still a strong reducing action; it appears to us that it should not be regarded as a glucoside (which TOLLENS does); apparently two alcoholic groups of the glucose have taken part in its formation,

the products of the reaction with acetic anhydride and benzoyl chloride could not as yet be obtained in a crystalline form.

They are not liable to fermentation but do not prevent the fermentation of any free glucose, although they retard the same.

The simultaneous formation of various isomeric mono- and diformal-glucosides may, as will be easily seen, explain the unsatisfactory result.

Galactose yielded products comparable with those obtained from glucose. The indistinctly crystalline methylenegalactoside (monoformal derivative) seems, however, to be a pure substance as the melting point (203) remained unaltered; $[\alpha]_D$ (in 2% aqueous solution) = $+124.8$. It is still being investigated.

Fructose yields a well-crystallised formalmethylenefructoside; when preparing the same a 50% sulphuric acid should be used. Melting point 92° ; $[\alpha]_D$ (2% aqueous solution) = -34.9 .

l-Sorbose yields a derivative melting at 54° and $[\alpha]_D$ (2% aqueous solution) = -25° . Rhamnose yields a product melting at 76° and $[\alpha]_D$ [0.4% aqueous solution] = -18° ; mannose also yields a crystalline derivative.

The (mono)methyleneglucosides also derive a certain importance from the analogy which they show, as regards their properties, with ordinary canesugar. In the same way as the latter has been formed from glucose and fructose, they are also formed, with the loss of two carbonyl groups, from two aldehydes from which one mol. of water has been eliminated. The reducing power is lost; towards phenylhydrazine they have become indifferent. On boiling with dilute acids, however, the components are regenerated.

It cannot be a matter of astonishment that the methylglucosides are quite as capable as the hexites, the oxy-acids and the sugars to give condensation products with formaldehyde. They are formed in abundance by simply melting the powdered glucosides with dry trioxymethylene.

In a properly crystallised state were obtained the formalderivatives of methylmannoside [m.p. 127° , $[\alpha]_D = +10.5$], of β -methyl-*l*-glucoside m. p. 136° , inactive] and of α - and β -methyl-*l*-galactoside.

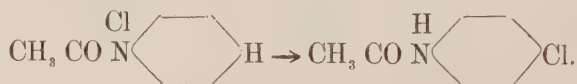
The derivatives of α -methyl-*l*-glucoside and of amyl- and aethyl-*l*-glucoside are viscous liquids.

It is worthy of notice that saccharose melted with trioxymethylene is decomposed with the formation of a mixture of formalderivatives of glucose and fructose, from which the latter was separated in a crystalline condition.

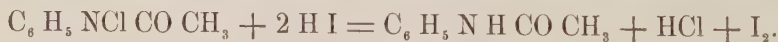
Chemistry. — "*The intramolecular rearrangement in halogen-acetanilides and its velocity*". By Dr. J. J. BLANKSMA. (Communicated by Prof. LOBRY DE BRUYN).

In a former paper ¹⁾ attention was called to the fact that the ready bromination, nitration, sulphonation etc. of phenol and aniline derivatives may be explained by assuming that the halogen atom or the groups NO₂ or SO₄H first enter the side-chain and then pass into the nucleus by intramolecular migration. Although a great many compounds are now already known containing groups linked to N or O which, under the influence of certain agencies, shift towards the nucleus, it was in these cases up to the present not proved with absolute certainty that we are really dealing here with a rearrangement of atoms or groups in a molecule and not with a reaction in which several molecules take part, which according to some authors is not improbable ²⁾. In order to investigate this it became necessary to know the velocity of reaction. If the reaction took place monomolecularly, we should be really dealing with an intramolecular displacement; a bimolecular reaction would point to a double decomposition between two molecules.

As a suitable example for this research, Prof. LOBRY DE BRUYN pointed out to me the conversion of acetylchloroanilide into parachloroacetanilide under the influence of hydrochloric acid, first discovered by BENDER ³⁾



It is known that the chlorine in acetylchloroanilide may be determined by adding potassiumiodide to its acetic acid solution and titrating the liberated iodine; *p*-chloroacetanilide does not react with K I:



The acetylchloroanilide was prepared according to the directions of CHATTAWAY and ORTON ⁴⁾ by shaking acetanilide with a solution of bleaching powder containing potassium bicarbonate. Within half a minute to a minute it will be noticed that the acetanilide has nearly entirely dissolved; after a few minutes the acetylchloroanilide separates in a crystalline state. CHATTAWAY and ORTON state that this

¹⁾ Proc. 25 Jan. and 29 March 1902.

²⁾ ARMSTRONG, Journ. Chem. Soc. **77**. 1053.

³⁾ Ber. **19**. 2273. SLOSSEN, Ber. **28**. 3265.

⁴⁾ Journ. Chem. Soc. **79**. 278.

compound is unstable and is spontaneously converted into *p*-chloroacetanilide. A closer investigation showed me that the cause of this must be attributed to the action of sunlight. After 14 days exposure to the light (May 14-28), the atmosphere being cloudy, this substance was entirely converted into *p*-chloroacetanilide while on a bright day in June the conversion was complete in a day. In the same manner it was shown that the analogous bromo-compound $C_6H_5NBrCOCH_3$ had been entirely converted after 3—4 hours exposure to direct sunlight on an afternoon in June and in 70 hours by exposure to incandescent gaslight; in diffuse daylight the conversion was complete after a few days, while both the chlorine and the bromine compound, could be preserved unaltered in the dark.

We therefore see that Br and Cl linked to N, shift to the nucleus under the influence of light. On consulting the literature it was found that BAMBERGER¹⁾ had already shown that phenylnitramine is converted by sunlight into *o*- and *p*-nitraniline, while he had also found that nitrosophenylhydroxylamine is very rapidly decomposed by direct sunlight and sometimes even explodes. The reaction takes here a more complicated course, the first stage of the reaction is probably the migration of the NO group to the nucleus.

Recently KNIPSCHER²⁾ has shown that azoxybenzene is converted by direct sunlight into *o*-oxyazobenzene.

We therefore see that under the influence of sunlight Br, Cl, NO₂, NO and O attached to N migrate from the side-chain to the nucleus and change place with an atom of hydrogen³⁾.

In the previous communication (i.e.) attention was called to the analogy of the CH₃-group with NH₂ and OH. Now however, we notice a difference. Whereas sunlight promotes the entering of atoms or groups into the nucleus of the NH₂-derivatives, it causes the formation of Br and Cl compounds in the side-chain of the CH₃-derivatives, for instance in the bromination or chlorination of toluene⁴⁾.

We may briefly refer to the experiments of SRPEK⁵⁾ and ERRARA⁶⁾ who have proved that on chlorinating parabromotoluene *p*-bromo-

1) Berichte **27**, 364, 1554, **34**, 66.

2) Proc. 31 May 1902.

3) No experiments showing the effect of light have, as yet, been made with phenol derivatives containing atoms or groups attached to the oxygen. It is probable that sunlight will in this case also exercise an influence on the migration of atoms or groups of the side-chain to the nucleus. This should be borne in mind when preparing these compounds.

4) SCHRAMM, Ber. **18**, 608.

5) Monatsch. f. Chem. **11**, 431.

6) Gazz. Chim. Ital. **17**, 202.

benzylbromide is formed in addition to *p*-bromobenzylchloride; in this case the bromine leaves the nucleus and is introduced into the side-chain¹⁾. This question merits further investigation.

After several preliminary experiments which showed that the interchange of Cl and H is much promoted by the catalytical action of acids, I determined the velocity of reaction in the following manner. 3—4 grams of the acetylchloroanilide were dissolved in 100 grams of glacial acetic acid (100%), 10 cc. of hydrochloric acid containing 2,9127 grams of HCl were added and finally the liquid was diluted with water to 500 cc. This solution was put into a black bottle and kept in a thermostat at 25°. As soon as the temperature had reached 25° 50 cc. were removed with a pipette and delivered into 100 cc. of water to stop the reaction. Excess of solution of potassium-iodide was added and the liberated iodine titrated with sodium thiosulphate (0,150 N). The following results were obtained.

<i>t</i> in hours.	cc. Na ₂ S ₂ O ₃ .	<i>k</i> .
0	49.3	
1/2	42	0.160
1	35.6	0.162
1 1/2	30.25	0.163
2	25.75	0.162
2 1/2	21.8	0.163
3	18.5	0.160
4	13.8	0.160
6	7.3	0.160
8	4.8	0.162

By applying the formula for the monomolecular reaction $k = \frac{1}{t} \ln \frac{A}{A-x}$

values are found for *k* which may be regarded as constants.

This proves that the reaction is really monomolecular and that we are dealing with an actual intramolecular rearrangement of atoms.

If instead of 10 cc., 20 cc. of hydrochloric acid were added the value for *k* was found to be 0.610; (the average result of eight observations); by using double the quantity of acid the velocity has therefore increased nearly four times. If instead of hydrochloric acid sulphuric acid of the same concentration was used, the conversion was very slow and a good constant was not obtained (32.8 cc. of Na₂S₂O₃ at first, 29 cc. after 24 hours).

In glacial acetic acid (99—100 %) the reaction takes place much

¹⁾ Cf. HANZSCH, Ber. **30**, 2334. THÖL and ECKEL, Ber. **26**, 1104.

more rapidly so that addition of very little hydrochloric acid suffices for the complete conversion.

The substance was again dissolved in glacial acetic acid and 3 cc. of a solution of dry hydrogenchloride in glacial acetic acid were added. The quantity of HCl thus introduced into 500 cc. of the solution amounted to only 0.0135 gram or not quite $\frac{1}{2000}$ part of the quantity present in the experiment with aqueous acetic acid.

The progressive change of the reaction was as follows:

<i>t</i> in hours	cc. Na ₂ S ₂ O ₃
0	30.3
$\frac{1}{2}$	29.7
1	28
$1\frac{1}{2}$	24
2	22.6
$2\frac{1}{2}$	19.8
3	17.2
$3\frac{1}{2}$	14.2
4	12.4
$4\frac{1}{2}$	10.5

On calculating *k* according to the formula $k = \frac{1}{t} l \frac{A}{A-x}$ it will

be seen that it keeps on increasing; this shows that the amount of the catalyser increases. On repeating the experiment it was found that, after the reaction, more hydrochloric acid existed (weighed as Ag Cl) than corresponded with the quantity added.

A graphic representation of the above figures plainly shows that we are dealing here with a reaction the velocity of which has been accelerated by an increase of the catalyser¹⁾. In the experiment with 20 per cent acetic acid the small increase of the relatively large amount of HCl is not perceptible.

Even when we do not add hydrochloric acid but set the acetic acid solution aside in the dark we meet with the same type of progressive change of the reaction. 10 c.c. of a solution in glacial acetic acid were titrated from day to day and took :

13. 12. 9. 6,7 3,7 2,6 1,5 and 1 c.c. Na₂ S₂ O₃

which figures again reveal the character of a reaction accelerated by a catalyser. It moreover shows that it is not the glacial acetic acid which starts and continues the reaction, but that the conversion is due to the catalyser formed from the product itself; in the first

¹⁾ OSTWALD, Lehrb. d. allgem. Chem. Bd. II, T. II, 266.

case it ought to be possible to calculate a constant by means of the formula employed for monomolecular reactions.

We are, therefore, dealing here with a case quite analogous to that of the spontaneous decomposition of alkyl sulphuric acid and nitrocellulose mentioned by OSTWALD; it is known that this may be prevented by adding a little K_2CO_3 or $CaCO_3$,

The reaction in the presence of alcohol takes place in a similar manner; on warming on the waterbath it may according to CHATTAWAY and ORTON become so violent that the alcohol begins to boil. This may be prevented by adding a trace of Na_2CO_3 which fact has been noticed by ARMSTRONG (l. c.).

We therefore, see :

1. That the conversion of acetylchloroacetanilide into *p*-chloroacetanilide proceeds like a monomolecular reaction and that it represents a true intramolecular rearrangement of atoms. It may therefore be compared to the case of the transformation of the bromo-amides under the influence of alkalis studied by VAN DAM and ABERSON¹⁾.

2. That Br, Cl, NO_2 , NO, and O attached to N change place, under the influence of sunlight, with an H-atom present in the nucleus.

3. That the conversion of acetylchloroacetanilide in alcoholic or acetic acid solution is caused by the formation of a catalyser which causes the reaction to proceed at an increasing rate (particularly in sunlight); this may be prevented by adding a trace of sodium carbonate or acetate as this removes the catalyser.

The investigation will be continued in various directions.

Chemistry. — "*Galvanic cells and the phase rule.*" By Dr. W. REINDERS of Breda. (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM).

NERNST²⁾ and, more recently, BANCROFT³⁾ have tried to establish a relation between galvanic cells, consisting of a combination of two metals surrounded by electrolytes in communication with each other, and the phase rule. Neither of them, however has paid sufficient attention to the fact that: When the phase *A* is in equilibrium with *B* and also with *C*, then *B* must be also in equilibrium with *C*. They regard the liquid electrolyte, in contact with the metals, as one homogeneous phase, whilst in reality two phases exist which are

¹⁾ Recueil **19**. 318 (1900).

²⁾ Theor. Chem. 1e Aufl. p. 560, 3e Aufl. p. 660.

³⁾ J. of phys. Ch. II 427 (1898).

not in equilibrium with each other; in fact various means are employed to prevent them from forming a homogeneous mixture.

The following contains a new effort to study the galvanic cell from the point of view of phase rule.

Those cells have been considered, which consist of a combination of 2 metallic electrodes, each surrounded by an electrolyte, containing the cation of the metal and connected with each other either directly or by means of an electrolyte.

Equilibrium may exist between both the electrodes and the surrounding electrolyte and when that equilibrium is reached, there exists at the plane of separation a certain potential difference, which is the measure of the energy required to transfer an equivalent of the metal from the one phase into the other.

BANCROFT is therefore in error in regarding the E.F. as an independent variable, as a further condition of equilibrium. He says: "In addition to the ordinary conditions of equilibrium there is also the electromotive force."

The variables would then be the n components, temperature, pressure and the potential difference and from this it would follow that for an invariant system $n + 3$ phases were required.

This is not the case, for π is completely defined when n phases are present in a system of n components at a given temperature and pressure (for instance by the formula of NERNST when $n = 2$ or 3).

There exists, however, no equilibrium between the two electrolytes in the cell. They will tend to form a homogeneous mixture in which case the composition is changed and the equilibrium with the electrode disturbed.

Therefore, there can be no question of a real equilibrium in the whole of the cell so long as both electrodes cannot be in equilibrium with the same electrolyte and the EMF becomes zero. An apparent equilibrium may, however, be got by preventing as much as possible the diffusion of the two electrolytes.

Considering the cell as a combination of two systems consisting of metal and electrolyte, the equilibrium of the separate systems should be discussed before alluding to that existing in the cell.

The equilibrium between the metallic electrode and the surrounding electrolyte and the potential difference at their plane of separation.

A. *The electrode consists of a single metal and the surrounding electrolyte also contains cations of that metal alone.*

When the electrolyte is a fused salt of the metal, we have a system of 2 components in 2 phases which at a given temperature and press-

ure is completely defined. If the electrolyte is a solution of a salt of the metal, there will be 3 components and, therefore, the concentration must also be given. The potential difference is determined by the formula of NERNST: $\pi = \frac{RT}{n} l \frac{P}{p}$ in which P = the solution tension of the metal, p = the osmotic pressure of the cation and n = the valency of the metal.

B. *The electrolyte consists of two different metallic salts M_1Z and M_2Z and in the electrode both metals of these salts may be present.*

Assuming that the electrolyte forms one homogeneous phase, the following distinction may be made in the equilibria of the electrode and electrolyte.

I. *At the given temperature there is no reaction between the two metals; they form therefore neither a compound nor a liquid or solid solution.*

Starting from the electrolyte, containing only the salt M_1Z (fused or in solution), there is a series of electrolytes with an increasing amount of M_2Z , which can only be in equilibrium with M_1 , and another series, starting from M_2Z with increasing quantities of M_1Z , which are only in equilibrium with M_2 .

Where these two series meet, we have an electrolyte, which is in equilibrium with both M_1 and M_2 . When there is no solvent and we are consequently dealing with a fused salt mixture, there is only one electrolyte which satisfies this equilibrium. We then have 3 phases: electrolyte, M_1 and M_2 and 3 components M_1 , M_2 and the acid group Z . The equilibrium at a given t and p is, therefore, completely defined.

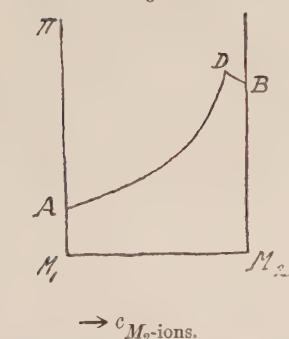
If, however, a solvent, and consequently a fourth component is also present, then, according to the quantity of this solvent, there will be a series of electrolytes which satisfy the conditions of equilibrium.

To follow the change in the potential difference, we may imagine, that a part of the ions M_1 in the electrolyte containing M_1Z , has been replaced by M_2 , but in such a way, that the total concentration of the ions $M_1 + M_2$ remains constant. The potential difference between M_1 and the electrolyte will increase, because in the equation

$\pi_1 = \frac{RT}{n_1} l \frac{P_1}{p_1}$, p_1 becomes smaller and consequently π_1 becomes greater.

The same applies to π_2 , the potential difference between the metal M_2 and an electrolyte containing only M_2 cations, when part of these ions is replaced by ions M_1 .

Fig. 1.



asymptotically approaches the ordinate M_2B , until it is intersected in D by the line BD .

In D the electrolyte is in equilibrium with the two metals M_1 and M_2 . To the left of it, M_1 is precipitated by M_2 , to its right, M_2 by M_1 . The condition of equilibrium in D is $\pi_1 = \pi_2$,

therefore
$$\frac{1}{n_1} \log \frac{P_I}{p_1} = \frac{1}{n_2} \log \frac{P_{II}}{p_2}$$

or

$$\sqrt[n_1]{\frac{P_I}{p_1}} = \sqrt[n_2]{\frac{P_{II}}{p_2}}$$

and, for metals of the same valency $P_I : P_{II} = p_1 : p_2$.

In words: in this equilibrium the ratio of the concentrations of the cations is equal to the ratio of the solution tensions of the metals.

Owing to the great difference in the solution tensions, p_1 must in most cases be very small and consequently the possibility of the second metal existing in contact with the mixed electrolyte, is limited to very minute concentrations of the first metallic salt; whereas the first metal may be in equilibrium with almost all the electrolytes, whatever the proportions of the two salts may be. The point D is, therefore, situated nearest to the less noble metal and almost coincides with B .

DANNEEL ¹⁾ has investigated an instance of this equilibrium, namely $2 \text{ HI} + 2 \text{ Ag} \rightleftharpoons 2 \text{ AgI} + \text{H}_2$. The solution, which is in equilibrium with both Ag and H_2 under 1 atm. pressure, is saturated with AgI ($c = 0,567 \times 10^{-8}$) and 0,043 normal in HI .

II. *The two metals form a homogeneous liquid or solid solution.*

This is the case with the liquid amalgams and other fused metals, with Zn—Ag ²⁾, Sb—Sn ³⁾ and other alloys.

¹⁾ Z. f. Phys. Ch. **33**, 415.

²⁾ HEYCOCK en NEVILLE. J. Chem. Soc. 1897, 415.

³⁾ HEYCOCK en NEVILLE. J. Chem. Soc. **330**, 387; VAN BULERT, Z. f. phys. Ch. **8**, 357 en REINDERS Z. f. anorg. Ch. **25**, 113.

Starting with the one pure metal and a solution, containing only the first metallic salt, it is found that on addition of the second metallic salt a small portion of the second metal will be separated and dissolved in the first one until the metallic phase is again in equilibrium with the electrolyte.

This equilibrium requires that $\pi_1 = \pi_2$ or for dilute solutions:

$$\frac{RT}{n_1} \log \frac{P_1}{p_1} = \frac{RT}{n_2} \log \frac{P_2}{p_2}$$

or also

$$\sqrt[n_1]{\frac{P_1}{p_1}} = \sqrt[n_2]{\frac{P_2}{p_2}}$$

in which P_1 and P_2 are the partial solution tensions of the two metals in the homogeneous metal phase. P_1 and P_2 are not constant here, but vary with the composition of the electrode.

This formula was obtained by NERNST¹⁾ and verified by Ogg²⁾ by means of the example $\text{Hg} + \text{AgNO}_3 \rightleftharpoons \text{HgNO}_3 + \text{Ag}$.

The electrode now contains both metals, as may also happen in the case of non-homogeneous mixtures (D in fig. 1). The difference, however, is that there the metals form 2 phases and here only one. If the electrolyte is a mixture of fused salts or a solution in which the total concentration of the two cations is constant, then, at a constant temperature and pressure, the system will still be monovariant and the relation $\sqrt[n_1]{P_1} : \sqrt[n_2]{P_2}$ or $\sqrt[n_1]{p_1} : \sqrt[n_2]{p_2}$ may still be variable. Once however, the relation $\sqrt[n_1]{p_1} : \sqrt[n_2]{p_2}$, that is the composition of the electrolyte, having been given, $\sqrt[n_1]{P_1} : \sqrt[n_2]{P_2}$ or the composition of the metal phase, is also determined and consequently also π .

At each temperature a series of two such coexisting phases are possible. The potential difference continuously changes with their composition.

In order to trace the general course of this π -line it must first be ascertained how P_1 and P_2 depend on the composition of the electrode.

If, in the metal phase, there are x atoms of M_2 and $1-x$ atoms of M_1 and x is small, the lowering of the solution tension may be taken as proportional to the number of dissolved molecules of the second metal, which is analogous to the lowering of the vapour pressure in liquid mixtures. If we call the solution tension of the pure metal M_1 P_1 , then $P_1 = P_I(1-x)$.

For small concentrations P_2 is proportional to the concentration

¹⁾ Z. für phys. Ch. **22**, 539.

²⁾ Z. für phys. Ch. **27**, 285.

of the second metal, as has already been proved by the investigations of MEYER ¹⁾, RICHARD and LEWIS ²⁾ and OGG ³⁾. Therefore $P_2 = Kx$.

The factor K is unknown. For $x = 1$ it becomes however $= P_{II}$. For small values of x however this is not necessarily the case, for it is to be expected that its value will be influenced by the nature of the first metal.

The condition of equilibrium then becomes:

$$\sqrt[n_1]{\frac{P_I(1-x)}{p_1}} = \sqrt[n_2]{\frac{Kx}{p_2}}$$

or

$$\frac{\sqrt[n_2]{p_2}}{\sqrt[n_1]{p_1}} = \frac{\sqrt[n_2]{Kx}}{\sqrt[n_1]{P_I(1-x)}}$$

and for $n_1 = n_2$

$$\frac{p_2}{p_1} = \frac{K}{P_I} \frac{x}{1-x}.$$

In words: The ratio of the ions in the electrolyte is to that of the atoms in the metal as $K : P_I$.

When the ratio $K : P_I$ is very great, $p_2 : p_1$ will also be great, even when x has but a small value, that is to say that the electrolyte will contain almost exclusively cations of the baser metal even when the concentration of that metal in the electrode is small.

In calculating the potential difference, the concentration of these ions (p_2) may, therefore, be taken as constant. $\pi = \frac{RT}{n_2} \ln \frac{Kx}{p_2}$ is then a logarithmic function of x and, for small values of x , will increase rapidly with it. $\left(\frac{d\pi}{dx} = \frac{RT}{n_2} \frac{1}{x} \right)$.

The graphic representation of this function is a curve rising rapidly from the potential of the nobler metal at a small distance from the π -axis. As x increases, K approaches to the value P_I , becoming equal to P_I when $x = 1$. The curve, therefore, bends sharply and after a small further rise reaches to the value of the potential of M_2 in a solution of pure M_2Z .

The ratio of the ions in the coexisting electrolyte $\frac{p_2}{p_1 + p_2}$ increases from 0 to nearly 1 for quite small values of x . The curve, which represents π as a function of this ratio, runs, therefore, at a slight incline towards the ordinate representing these baser metal, finally approaching it almost asymptotically.

¹⁾ Z. f. phys. Ch. 7, 477.

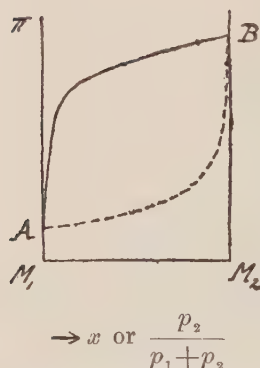
²⁾ " " " " 28, 1.

³⁾ l. c.

The same results are obtained by considering the equation

$$\pi = \frac{RT}{n_1} l \frac{P_1(1-x)}{p_1}$$

a. When the two metals form homogeneous mixtures in all proportions, the curves will therefore possess the general form shown in figure 2.

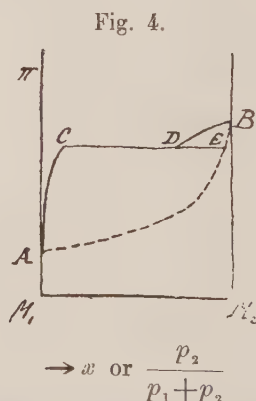
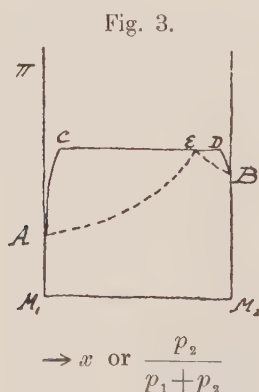


The points on these curves, which are situated on the same horizontal line, are co-existing phases. The ordinate of the points gives the potential difference at the plane of separation.

Although it is not impossible, a maximum or minimum will rarely occur, unless the solution tensions of the two components differ very little.

b. If the metals are not homogeneously miscible in every proportion, and the series of mixtures is therefore discontinuous, the two metallic phases, which are in equilibrium with each other (the end points of the break), will also be in equilibrium with the same electrolyte. The potential in this electrolyte must be the same for both metallic phases, for if such were not the case, a current might be generated and the equilibrium would be disturbed.

According to whether the potential difference in this non-variant equilibrium is greater than those of the pure metals in solutions of their salts or intermediate between them, the figures 3 or 4 are obtained.



C and *D* are the two metallic phases in equilibrium with each other. *E* is the coexisting electrolyte.

The case of fig. 3 becomes identical with that of fig. 1 if *C* and *D*

coincide to the right and the left with the π -axis, that is when the metals do not mix.

An example of the case of fig. 4 is found in my investigation ¹⁾ of the equilibrium between fused lead, zinc and their chlorides. At 515° is $C = 89\%$ of Pb, 11% of Zn; $D = 97\%$ of Zn, 3% of Pb; $E = 99,9\%$ of $ZnCl_2$, 0,1% of $PbCl_2$ and if π_A is taken as 0 then $\pi_{CED} = 0,277$ Volt and $\pi_B = 0,283$ Volt.

A second example is found in the cadmium amalgams, investigated by JAEGER ²⁾ and BIJL ³⁾. Further researches are those of MEYER and RICHARDS and LEWIS on the dilute amalgams, those of LINDECK ⁴⁾ and those of HERSCHKOWITSCH ⁵⁾, who met with the case represented by fig. 4 in his investigation of Cd—Sn, Cd—Pb, Zn—Sn, Zn—Bi, Cu—Ag.

In all these cases the concentration of the nobler metal in the electrolyte is very small; to a large extent the curve AEB almost coincides with M_2B .

III. *The two metals form a compound.*

If the compound is present in a pure condition there will only be 2 phases and at least 3 components. Even without solvent the system is still monovariant at constant temperature and pressure. As in case I, if one of the pure metals forms the electrode, a series of solutions exists with varying proportions of the salts M_1Z and M_2Z , which may be in equilibrium with this compound. The limit of this series is reached when the solutions are also in equilibrium with a second metallic phase (one of the pure components, a liquid or solid solution or a second compound).

In order to make use of NERNST's formula to calculate the potential difference, it is necessary to assume that the electrode forms ions of the same composition as the compound, for instance of Al_2 , Zn_2Ag , etc., and to substitute the concentration of these ions in the formula. The solution pressure is then a definite constant for this compound, as it is for every pure metal:

$$\text{therefore} \quad \pi = \frac{RT}{n_{1,2}} \ln \frac{P_{1,2}}{P_{1,2}}.$$

¹⁾ Z. f. anorg. Ch. **25** 126.

²⁾ Wied. Ann. **65** 106.

³⁾ Inaug. Dissert., Amsterdam 1901.

⁴⁾ Wied. Ann. **35** 311.

⁵⁾ Z. f. phys. Ch. **27** 123.

If the formula of the compound is $M_1^a M_2^b$, then owing to dissociation, ions M_1 and M_2 will occur along with ions $M_1^a M_2^b$ and between these an equilibrium will exist expressed by the equation:

$$p_1^a p_2^b = K p_{1,2}.$$

When the total concentration of the ions remains constant, $k - p_1$ may be substituted for p_2 and the equation becomes

$$p_1^a (k - p_1)^b = K p_{1,2}.$$

The maximum value of $p_{1,2}$ is reached when the first differential quotient with respect to $p_1 = 0$, that is, when

$$a p_1^{a-1} (k - p_1)^b - b p_1^a (k - p_1)^{b-1} = 0$$

or

$$a (k - p_1) = b p_1$$

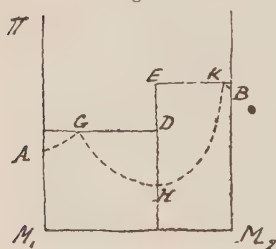
or

$$p_1 : p_2 = a : b.$$

$p_{1,2}$ therefore reaches a maximum and π a minimum where the ratio of the ions M_1 and M_2 in the electrolyte is equal to that of the metals in the compound.

a. If the compound can be in equilibrium with an electrolyte in which the ratio of the cathions is the same as that of the metals in the compound and if in addition to the compound only the metals in a pure condition are capable of existence, then the π -curve will have the form indicated in fig. 5.

Fig 5.



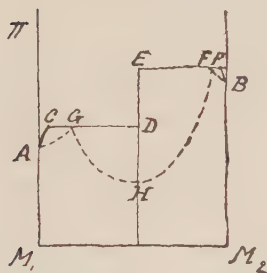
The points on the line AG give the compositions of electrolytes in equilibrium with pure M_1 and the corresponding potential differences. With the electrolyte G both M_1 and the compound are in equilibrium. So long as both metal phases are present, the potential difference remains constant. Should M_1 have entirely disappeared, so that the electrode consists of the pure compound (composition = D), the electrolyte may vary from G to K while the potential difference first falls to H and then again rises to K . In K there is again a non-variant equilibrium between the compound, pure M_2 and the electrolyte K and so long as these phases exist the potential difference remains constant. But when the compound has disappeared, it falls to B , while the electrolyte changes from K to pure M_2Z .

From an electrolyte having a composition situated between G and K the compound M_1M_2 is precipitated by M_1 and also by M_2 .

Owing to the small rise of the line AG , the first case is sure to occur but rarely, as the line GHK then stands a chance of not being again intersected by AG and this case will pass into that of b (see below).

H may be situated higher or lower than A .

Fig. 6.



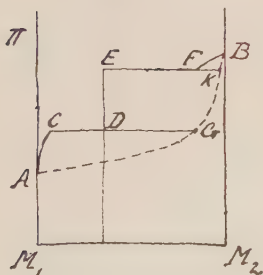
If, in addition to the compound, two solid solutions are possible (M_1 in which a little M_2 and M_2 in which a little M_1 is dissolved), the π -curve takes the course indicated in fig. 6, which differs from fig. 5 in this, that in presence of the electrolytes A to G pure M_1 is replaced by an electrode of varying composition, represented by the line AC , and in presence of the electrolytes B to K metallic phases B to F occur.

The line BF may either rise or fall ¹⁾.

An example of this case is probably the system Hg, Ag, NO_3 , examined by Ogg (l.c.) for dilute solutions of Ag in Hg .

b . If the compound cannot exist in presence of an electrolyte in which the ratio of the cations is the same as that of the atoms in the compound and if we consider the case in which in addition to the compound two solid solutions are possible, we get fig. 7.

Fig. 7.



Metallic phases from A to C are in equilibrium with electrolytes from A to G . From C to D the electrode consists of a mixture of the two phases C (a solution of M_2 in M_1) and D (the compound). The potential difference is constant.

As therefore, the compound is not in equilibrium with an electrolyte having the same ionic ratio, it will, in contact with such an electrolyte, dissolve with separation of M_1 , and tend towards the equilibrium G, D, C . If, before attaining this, D has totally dissolved, a metallic phase on the line AC and an electrolyte on the line AG will remain.

From D to E the pure compound is in equilibrium with an electrolyte of varying composition, situated on the line GK . The potential difference rises. The metallic phase F and the compound E are in equilibrium with the electrolyte K . As long as these three are present, the potential difference is constant. If, however, the electrode reaches a composition to the right of F , the compound will have disappeared

¹⁾ In fig. 6 to read K instead of F and F instead of P .

and there will be equilibrium of the metallic phases F to B with the electrolytes K to B . π rises or falls (as in fig. 3).

It may be expected here as in II, that the line $AGKB$ will to a large extent run close to the π -axis of M_2 and that in consequence the concentration in M_2 -ions in G and K will be very small.

When no solid mixtures of the two metals are possible AC and BF coincide with the π -axis. F then lies above B .

If there is more than one compound, the sudden change of potential DE is repeated for such compound. HERSCHKÖWITSCH (l.c.) has noticed these sudden rises with Zn_2Cu , Zn_4Ag , $ZnSb_2$, Cu_3Sn , Ag_4Sn and has regarded them as evidence of the existence of these compounds.

We should, however, be careful when drawing such conclusions as to the composition of alloys from measurements of potential difference, for an alloy, obtained by melting together the two components and rapidly cooling the mass, is a badly defined substance and often contains more than two phases which are not at all in equilibrium. When they are brought into contact with an electrolyte consisting of a salt of the less noble metal, the unstable compounds in the alloy may be converted into the more stable ones and this reaction, which is caused by a short circuited element (unstable compound, electrolyte, stable compound), continues until only the two phases, which are really in equilibrium, remain. During this period the EMF observed is not necessarily constant.

The constant cells.

As already stated, there is no equilibrium between the two electrolytes of a cell; they tend to form a homogeneous mixture by diffusion. The potential difference between two electrolytes is, however, generally very small and when the diffusion is small, it will change very little. As, moreover, the EMF of a cell consists of the sum of the potential differences between the two electrolytes and between electrolytes and the electrodes, an apparent equilibrium and consequently a constant EMF may be secured by making the diffusion as small as possible.

To attain this it is necessary that there should be equilibrium between the electrodes and their electrolytes. But, in a constant cell, that equilibrium must not be modified when the current is allowed to flow and an interchange between the phases takes place in consequence. At constant t and p the system must be invariant.

If the electrode consists of a single metal, the concentration of the ions of the metal in the electrolyte must be kept constant. In case

the electrolyte consists of a solution of the metallic salt, the presence of this salt in a third phase of constant composition, such as a solid hydrate, is required. These conditions are satisfied in the original form of the Clark cell, which contains on one side Zn and a saturated solution of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ and on the other side mercury and a saturated solution of Hg_2SO_4 .

If the electrode consists of two metals forming only one phase (liquid solution, solid solution or compound), the current will necessarily cause a change in the equilibrium, because the ratio of the metals in the electrolyte is generally different from that in the electrode. The equilibrium will only then become invariant when a second metallic phase appears.

If there is no solvent, and the electrolyte therefore consists of a mixture of the two fused metallic salts, its composition is completely defined by the presence of 3 phases of the 3 components (M_1 , M_2 and the common acid radicle). If, however, there is also a fourth component in the form of a solvent, a fourth phase must be present to make the equilibrium invariant such as the crystals of one of the two salts. The choice between the two salts is not an arbitrary one, but is regulated by the required relation of the concentration of the cations and the solubility of the two salts.

From this it follows, that on passing the current, only that metal, the salt of which is present in a second constant phase, can dissolve or deposit on the electrode (which consists of a mixture of the two metal phases). The ratio of the quantities of the two metallic phases must be regulated accordingly.

An example, from among the commonly used normal elements is the Weston cell in which the Cd-electrode consists of a mixture of a liquid phase (Hg with 5 % Cd) and a solid one (Hg with 14 % Cd)¹⁾ while the surrounding electrolyte consists of a solution of CdSO_4 and traces of Hg_2SO_4 , saturated with $\text{CdSO}_4 \cdot \frac{8}{3} \text{H}_2\text{O}$.

The Clark cell in which a zinc amalgam with 10—15% of zinc is used, is clearly a similar combination.

¹⁾ Byl. l. c.

Astronomy. — "*On the yearly periodicity of the rates of the Standardclock of the observatory at Leyden, HOHWÜ No. 17.*"
Second part. By Dr. E. F. VAN DE SANDE, BAKHUYZEN.

III. *The period 1862—1874.*

9. As was mentioned, several investigations about the rate of the clock HOHWÜ 17 during this period have been made by KAISER. They have been partly published. These published investigations are relative to the period 1862 May—1864 August ¹⁾.

Afterwards, in the autumn of 1870, KAISER undertook a new investigation founded on the period 1862—1870 ²⁾. In 1872 this investigation was continued and extended over the last year and a half ³⁾. KAISER was engaged in this investigation, the results of which were intended for the 3rd Volume of the Annals of the observatory, till the last months of his life. It was unfinished, however, at his death.

The results which KAISER had obtained did not wholly satisfy him. Several singular irregularities had shown themselves; moreover he was aware of the fact that the barometer-readings, one of the foundations of the investigation, might still be affected by rather considerable systematic errors, even after they had been corrected as well as possible. These barometer-readings had been derived by him from observations repeated three times every day on an old defective mercury barometer of BUTTI hanging in his study (during a year and a half on an Aneroid-barometer). The correction of this barometer was derived from simultaneous readings of the barometer in the transit-room. It appeared to be variable with the height of the barometer and increased considerably in the course of the years; moreover the temperature of the barometer was quite uncertain.

For these reasons H. G. VAN DE SANDE BAKHUYZEN, when in 1873 he planned the continuation of the investigation of the clock, deemed it necessary, first of all to procure better data about the atmospheric pressure to which the clock had been exposed ⁴⁾. He intended to derive these by the help of the regular barometer-readings made at the meteorological Institute at Utrecht.

In the first place the constant differences between the barometer-readings at Utrecht and those at Leyden (the barometer in the transit-room) had to be derived. From extensive calculations, which have

¹⁾ F. KAISER l. c.

²⁾ *Vide*: Verslag van den staat der sterrenwacht te Leiden. 1870—71 pp. 15 and 16.

³⁾ *Vide*: Verslag van den staat der sterrenwacht te Leiden. 1871—72 pp. 14 and 15.

⁴⁾ *Vide*: Verslag van den staat der sterrenwacht te Leiden 1872—73 p. 4.

been continued afterwards, it finally appeared that, when the necessary corrections ¹⁾ and the reduction for difference in altitude had been applied, the mean barometer-readings at both places are in perfect agreement ²⁾.

After the completion of this preparatory work H. G. VAN DE SANDE BAKHUYZEN has been prevented by want of time from further investigations of the rates of the clock Hohwü 17.

10. When last year the investigation of the clock in the period 1862—74, was resumed by me, I have soon given up the attempt to derive trustworthy corrections for the barometer of BUTTI and I too have used the readings at Utrecht. It appeared that in this way we can get a precision sufficient for our purpose, at least for the mean monthly barometer-readings.

I had at my disposal readings of the barometer at Utrecht for 20^h, 2^h and 10^h. From these I derived mean barometer-readings reduced to 0° for the whole of our period ³⁾. In addition to these, however, we have readings of the barometer at Leyden for the last months. For, to begin with July 1873, the barometer in the transit-room has been regularly read five times a day. From these I could derive, in the same way as I had done for the time after 1877 mean barometer-readings, which afterwards I reduced to 0°. The comparison of the monthly means obtained in the two ways stands as follows :

	L. — U.		L. — U.
1873 July	+ 0.3 Mm.	1873 Dec.	+ 0.3 Mm.
Aug.	0.0	1874 Jan.	— 0.2
Sept.	— 0.2	Febr.	+ 0.2
Oct.	— 0.2	March	+ 0.3
Nov.	— 0.1	April	+ 0.1

The differences thus appear to be very small. They would have turned out still smaller perhaps, if we had not neglected the hundredth parts of the millimeters in all the computations. The mean value amounts only to + 0,05 Mm.

¹⁾ About the errors of the barometer at Utrecht see: J. D. VAN DER PLAATS, „Over den barometer van het K. Nederl. Meteor. Inst.” (Meteor. Jaarboek voor 1888). At Leyden the barometer-readings were reduced to those of the standard-barometer of FUESS.

²⁾ See also: *Annalen der Sternwarte in Leiden*. Vol. VI pp. CXIV—CXVI.

³⁾ By taking the means of the readings at 10^h, 20^h, 2^h, 10^h and giving half weight to both the extreme values I obtained the daily means from midnight to midnight.

11. For the derivation of the temperature of the clock I had the following data at my disposal.

From 1862 to 1866 May a thermometer hanging at the pier of the clock was read at 8^h 30^m in the morning.

Beginning from that time two thermometers suspended in the clock case were regularly read, but from 1866 June to 1873 June these readings were only made at 8^h 30^m in the morning. Since 1873 July both thermometers were read five times a day.

From July 1873 it was possible therefore to take daily means of the temperature according to the upper thermometer in the clock case in the same way as was done for the time after 1877.

For former periods I had to find corrections in order to reduce to daily means of the latter thermometer.

For the purpose of finding these corrections I compared :

1st. For the years 1871, 1872 and 1873 the readings at 8^h 30^m in the morning of the upper thermometer in the clock case with those of the thermometer at the clockpier ;

2nd. for the years 1873—75 the readings at 8^h in the morning of the upper thermometer in the clock case with their daily means.

From the two comparisons I found the following monthly means of the differences Δ_1 = clock case — pier and Δ_2 = daily means — readings at 8^h, everything being expressed in degrees RÉAUMUR. The index-corrections have been taken into account.

	Δ_1	Δ_2		Δ_1	Δ_2
Jan.	+ 0.21	+ 0.22	July	+ 0.01	+ 0.36
Febr.	.11	.19	Aug.	.19	.41
March	.14	.44	Sept.	.16	.46
April	.15	.48	Oct.	.20	.26
May	.06	.38	Nov.	.16	.29
June	.03	.47	Dec.	.16	.04

For all the months I adopted for Δ_1 the general mean + 0.13. For Δ_2 I adopted

October—February + 0.20
March—September + 0.43

With the aid of these values and of the index-errors determined at regular intervals the necessary reductions were applied.

Lastly I compared the temperatures according to the upper and lower thermometer, as has been done for the subsequent period,

the difference in the two cases being that, for the period now under discussion, the clock was only enclosed in a single case. I will set down only the results which I found for the means of the 5 daily readings in the years 1873—76.

	u.—l.		u.—l.
Jan.	+ 0.32	July	+ 0.44
Febr.	+ 0.34	Aug.	+ 0.40
March	+ 0.38	Sept.	+ 0.34
April	+ 0.42	Oct.	+ 0.30
May	+ 0.44	Nov.	+ 0.31
June	+ 0.44	Dec.	+ 0.31

These differences are corrected for index-errors.

12. With a few exceptions I used for the time before 1872 the same time-determinations from which KAISER had formed his monthly means of the rates. Some corrections however could be applied. The clock had been set going in June 1861 but I left out the first year and placed the beginning of my investigation at 1862 May, as KAISER had done. It ends April 1874, a short time before the occurrence of the perturbation.

The observed rates were first reduced to 760 Mm. at 0° and to $+10^{\circ}$ R. For the coefficient b I again took $+0.0140$ (KAISER in his last investigation found $+0.0134$) and for c I adopted the value -0.0174 which is the mean result of KAISER's last investigation, allowance being made for the fact that I now reduced the barometer-readings to 0° .

In the following table all the columns have the same meaning as the corresponding ones in the table for the period 1877—1898.

	Obs ^d D. R.	Bar.	Temp.	Red ^d D. R. I	Red ^d D. R. II	O.—C.
1862 May	— 0.322 ^s	759.5	+ 12.7	— 0.268 ^s	— 0.299 ^s	+ 15
June	0.390	58.2	13.0	0.313	333	— 19
July	0.408	60.3	13.8	0.346	350	— 36
Aug.	0.424	60.6	14.5	0.354	341	— 27
Sept.	0.328	62.9	13.0	0.317	290	+ 24
Oct.	0.346	59.4	10.6	0.328	294	+ 20
Nov.	0.245	60.0	6.2	0.311	280	+ 34
Dec.	0.192	61.6	5.0	0.301	281	+ 33
1863 Jan.	0.301	56.9	4.8	0.348	344	— 30
Febr.	0.141	69.1	5.2	0.352	365	— 51
March	0.246	58.4	6.4	0.287	314	0
April	0.237	61.0	8.8	0.272	306	+ 8
May	0.213	61.7	10.8	0.223	254	+ 60
June	0.388	59.9	13.6	0.324	344	— 30
July	0.247	64.3	14.2	0.234	238	+ 76
Aug.	0.415	60.1	15.1	0.327	314	0
Sept.	0.404	58.2	11.8	0.348	321	— 7
Oct.	0.442	58.8	10.3	0.420	386	— 72
Nov.	0.237	63.9	6.4	0.355	324	— 10
Dec.	— 0.277	63.1	6.0	0.390	370	— 56
1864 Jan.	+ 0.032	68.8	0.8	0.251	247	+ 67
Febr.	— 0.165	59.8	2.2	0.298	311	+ 4
March	0.305	54.0	5.1	0.306	333	— 18
April	0.121	63.9	6.9	0.230	264	+ 51
May	0.208	61.4	10.1	0.226	257	+ 59
June	0.342	60.2	12.7	0.298	318	+ 2
July	0.375	62.0	13.9	0.335	339	— 13
Aug.	0.347	63.2	13.2	0.336	323	+ 9
Sept.	0.401	61.2	12.5	0.374	347	— 9
Oct.	0.369	59.0	8.7	0.378	344	0
Nov.	0.268	58.8	4.6	0.345	314	+ 35
Dec.	0.163	63.8	1.2	[0.369]	370	— 15

	Obsd D. R.	Bar.	Temp.	Redd D. R. I	Redd D. R. II	O.—C.
1865 Jan.	— ^s 0 433	750.0	+ 2.4	— ^s 0.425	— ^s 0.421	— 60
Febr.	0.210	59.5	1.1	0.358	371	— 5
March	0.264	57.9	2.7	0.362	389	— 17
April	0.278	65.2	8.6	0.375	409	— 31
May	0.390	61.1	12.3	0.365	396	— 12
June	0.352	65.3	12.6	0.381	401	— 11
July	0.464	61.2	15.4	0.387	391	+ 5
Aug.	0.487	59.0	14.0	0.403	390	+ 11
Sept.	0.389	68.2	14.1	0.433	406	+ 1
Oct.	0.485	53.3	9.5	0.400	366	+ 46
Nov.	0.376	60.1	6.5	0.438	407	+ 11
Dec.	0.237	68.6	4.1	0.460	440	— 17
1866 Jan.	0.366	58.7	5.1	0.433	429	— 2
Febr.	0.473	54.4	4.7	0.487	500	— 69
March	0.425	54.3	4.8	0.435	462	— 27
April	0.394	60.2	8.4	0.425	459	— 21
May	0.347	61.7	9.2	0.385	416	+ 25
June	0.479	60.2	14.9	0.397	417	+ 26
July	0.477	59.9	14.1	0.405	409	+ 35
Aug.	0.536	56.6	13.3	0.431	418	+ 27
Sept.	0.599	56.7	12.5	0.509	482	— 36
Oct.	0.392	64.9	9.1	0.477	443	+ 3
Nov.	0.421	58.6	7.1	0.451	420	+ 26
Dec.	0.351	60.6	5.2	0.443	423	+ 23
1867 Jan.	0.376	52.9	2.2	0.413	409	+ 36
Febr.	0.285	64.4	5.5	0.425	438	+ 7
March	0.407	56.2	3.8	0.462	489	— 45
April	0.457	55.9	7.8	0.438	472	— 29
May	0.396	59.8	10.4	0.386	417	+ 25
June	0.413	63.4	13.0	0.409	429	+ 11
July	0.497	59.1	13.3	0.427	431	+ 7
Aug.	0.505	62.2	14.4	0.459	446	— 10

	Obs ^d D. R.	Bar.	Temp.	Red ^d D. R. I	Red ^d D. R. II	O.—C.
1867 Sept.	— 0.484 ^s	763 7	+ 13.2	— 0.480 ^s	— 0.453 ^s	— 19
Oct.	0.455	59.4	8.9	0.466	432	0
Nov.	0.312	65 9	6.4	0.458	427	+ 2
Dec.	0.266	62.2	3.1	0.417	397	+ 30
1868 Jan.	0.288	58.9	2.1	0.410	406	+ 19
Febr.	0.298	64.6	4.9	0.451	464	— 41
March	0.302	60.6	5.8	0.383	410	+ 11
April	0.344	60.4	7.4	0.395	429	— 10
May	0.359	62.6	12 5	0.351	382	+ 35
June	0.396	65.6	14.0	0.404	424	— 9
July	0.493	62.4	16 5	0.414	418	— 5
Aug.	0.592	60.0	16.1	0.486	473	— 62
Sept.	0.510	59.3	13.2	0.444	417	— 8
Oct.	0.381	60 3	8.4	0.413	379	+ 28
Nov.	0.263	61.7	5.6	0.364	333	+ 71
Dec.	0.421	52.4	5 9	0.386	336	+ 36
1869 Jan.	0.237	63.7	2.9	0.413	409	— 9
Febr.	0.269	60 9	5.7	0.357	370	+ 28
March	0.318	56.4	3.7	0 378	405	— 9
April	0.336	62.4	8.8	0.391	425	— 31
May	0.383	57.2	9.9	0.346	377	+ 14
June	0.358	63.0	11.0	0.383	403	— 14
July	0.415	64.2	14.4	0 397	401	— 14
Aug.	0.420	64.2	13.6	0.416	403	— 18
Sept.	0.456	58.0	12 8	0.379	352	+ 31
Oct.	0.409	61.3	9.2	0.441	407	— 26
Nov.	0.340	58.6	6.0	0.390	359	+ 20
Dec.	0.349	56.5	2 9	0.424	404	— 27
1870 Jan.	0.202	62.7	3.1	0.360	356	+ 19
Febr.	0.132	60.0	0.9	[0.290]	344	+ 29
March	0.280	61.6	3.9	0.408	435	— 63
April	0 226	65.1	7.7	0 337	371	0

	Obs ^d D. R.	Bar.	Temp.	Red ^d D. R. I	Red ^d D. R. II	O.—C.
1870 May	— 0 ^s 299	763.4	+ 9.9	— 0 ^s 349	— 0 ^s 380	— 40
June	0.352	63.9	12.5	0.363	383	— 14
July	0.457	61.1	14.9	0.387	391	— 23
Aug.	0.536	58.5	14.4	0.438	425	— 58
Sept.	0.344	64.4	11.4	0.379	352	+ 14
Oct.	0.475	54.7	8.9	0.420	386	— 21
Nov.	0.388	56.3	5.9	0.407	376	— 12
Dec.	0.217	59.5	1.8	[0.353]	366	— 3
1871 Jan.	0.167	58.9	0.1	0.324	320	+ 42
Febr.	0.114	63.5	2.5	0.293	306	+ 55
March	0.198	62.7	6.0	0.306	333	+ 28
April	0.348	57.6	7.2	0.363	397	— 36
May	0.250	63.2	9.1	0.311	342	+ 18
June	0.391	58.9	11.6	0.348	368	— 8
July	0.458	58.7	14.0	0.370	374	— 14
Aug.	0.427	62.9	15.0	0.381	368	— 8
Sept.	0.475	59.3	12.8	0.416	389	— 29
Oct.	0.357	61.7	7.6	0.423	389	— 29
Nov.	0.309	60.9	3.7	0.432	401	— 41
Dec.	0.178	64.5	2.1	0.378	358	+ 2
1872 Jan.	0.285	54.6	3.6	0.320	316	+ 44
Febr.	0.273	59.8	4.5	0.366	379	— 19
March	0.294	57.4	5.9	0.329	356	+ 4
April	0.317	58.7	8.2	0.330	364	— 4
May	0.344	59.5	9.6	0.344	375	— 15
June	0.385	60.4	13.1	0.337	357	+ 3
July	0.400	60.7	15.5	0.314	318	+ 42
Aug.	0.430	60.4	14.6	0.356	343	+ 17
Sept.	0.464	57.6	13.1	0.376	349	+ 11
Oct.	0.430	55.8	8.8	0.392	358	+ 2
Nov.	0.417	55.3	6.9	0.405	374	— 14
Dec.	0.377	52.3	5.1	0.354	334	+ 26

	Obsd D. R.	Bar.	Temp.	Redd D. R. I	Redd D. R. II	O.—C.
1873 Jan.	— 0.301 ^s	757.6	+ 4.5	— 0.368 ^s	— 0.359 ^s	+ 1
Febr.	0.208	63.6	2.3	0.392	405	— 45
March	0.249	57.5	4.8	0.304	331	+ 29
April	0.263	59.8	7.5	0.304	338	+ 22
May	0.310	60.1	8.7	0.334	365	— 5
June	0.337	60.9	12.7	0.303	323	+ 37
July	0.405	61.2	14.8	0.338	342	+ 18
Aug.	0.429	60.7	14.6	0.359	346	+ 14
Sept.	0.406	60.5	11.5	0.387	360	0
Oct.	0.426	58.0	9.7	0.403	369	— 9
Nov.	0.352	59.2	5.9	0.412	381	— 21
Dec.	0.493	69.2	5.0	0.409	389	— 29
1874 Jan.	0.253	63.0	4.3	0.394	390	— 30
Febr.	0.180	63.8	3.6	0.344	357	+ 3
March	0.168	65.8	5.5	0.327	354	+ 6
April	0.275	59.0	8.5	0.287	321	+ 39

Before I undertook the further investigation of the reduced rates I¹⁾ I tried to find out the relation of the rates below 0° to those above that temperature. It appeared that a systematic deviation of the former is far less evident than it was in the period 1877—98. In fact such a deviation shows itself clearly only in the two months 1870 February and December. Finally I excluded the days with temperatures below 0° only for these months and for 1864 December²⁾.

The modified reduced rates I, together with the corresponding temperatures, are as follows:

	Temp.	Red. D. R. I.
1864 December	+ 2.4	— 0 ^s .390
1870 February	+ 1.9	— 0.331
December	+ 3.6	— 0.386

¹⁾ In comparing my values of the reduced rates I for the two first years with those occurring in KAISER's papers, allowance must be made for the fact that my values apply for a pressure of 760 Mm. at 0°, whereas those of KAISER may be assumed to apply for a barometer-height of 760 Mm. at +10°.

²⁾ During 8 other months the deviations were small and variable in sign.

13. In the first place I have investigated in how far the non-periodic part of the rate, the constant α , has varied during the period under consideration.

For this purpose I have combined the monthly means to yearly means. They are as follows, the years beginning with May.

1862	— 0.316	1868	— 0.400
1863	.309	1869	.384
1864	.350	1870	.368
1865	.421	1871	.367
1866	.436	1872	.353
1867	.428	1873	.358

It is seen that the negative rate has somewhat increased in the beginning and somewhat decreased afterwards and that it remained nearly constant during the last four years.

With these values and the corresponding ones for years beginning with August, November and February, I drew, in the same way as was done for the period formerly considered, a curve representing in a first approximation the change of α with the time.

14. In the second place the influence of the temperature was investigated. I tried to find out:

1st. In how far, if we assume a linear influence of the temperature, the adopted temperature-coefficient applies for the whole of the period;

2nd. whether there is any term varying as the square of the temperature.

For the first investigation the several years were kept separate. They were assumed to begin with February.

I used 1st. the deviations of the monthly means from their yearly mean, 2nd. the deviations of these same monthly means from the values of α taken from the curve. In the third and fourth place the computations were repeated using, not the monthly means themselves, but the mean value for the first month combined with the last, that for the second combined with the last but one, etc.. By this device the influence of the "supplementary term" must be nearly completely eliminated at the outset.

In this way I found for the correction of the adopted coefficient — 0.0174, the following four series of values; they are expressed in tenthousandth parts of a second.

	I	II	III	IV
1863	+ 5	+ 4	+ 9	+ 9
1864	+ 28	+ 10	+ 13	0
1865	+ 1	+ 4	+ 6	+ 7
1866	+ 14	+ 17	+ 10	+ 14
1867	— 11	— 6	— 11	— 10
1868	— 26	— 23	— 31	— 32
1869	— 11	— 11	— 15	— 17
1870	— 33	— 28	— 38	— 35
1871	— 26	— 27	— 41	— 41
1872	+ 20	+ 18	+ 15	+ 12
1873	+ 33	+ 35	+ 29	+ 31

The results of the four computations are nearly accordant. The value of the temperature coefficient appears to have varied far less than it did subsequently. A small fluctuation however, of the same nature as that which existed afterwards, appears to have occurred. It might be allowable to assume, in accordance with the second computation, which in my opinion is to be preferred :

1863—66	$\Delta c = + 9$	$c = - 0.0165$
1867—71	— 19	— 0.0193
1872—73	+ 26	— 0.0148

From all the years together we should find

$$1863-73 \quad \Delta c = - 1 \quad c = - 0.0175$$

The investigation about the existence of a quadratic term I only executed for the mean of the 11 years.

For this purpose I used the deviations according to the second and fourth computation.

If Δc_1 and c_2 represent the correction of the coefficient of $t-t_0$ and the coefficient of $(t-t_0)^2$, t_0 being the mean temperature ($= + 8^{\circ}.6$ R.), we have, expressing both in ten thousandth parts of the second as unit,

	Δc_1	c_2
2 nd Comp.	+ 0.5	— 0.92
4 th " "	— 6.2	— 0.43

At least for the mean of the 11 years, therefore, a quadratic term must be quite insensible.

15. It seemed unnecessary to apply corrections to the reduced rates I on account of the temperature coefficient, before proceeding to the investigation of the supplementary term. For the mean value of

this coefficient agrees all but absolutely with the value originally adopted and its fluctuations are certainly inconsiderable.

I made use of the deviations of the monthly means from the values of α taken from the curve and I made the years begin with May.

For the sake of brevity I will only give the mean results for 4 groups, each of three years. In the last column the general means are set down.

	62—64	65—67	68—70	71—73	1862—1873
May.....	+ 76	+ 44	+ 46	+ 29	+ 48
June	+ 4	+ 29	+ 9	+ 30	+ 18
July.....	+ 12	+ 20	— 9	+ 19	+ 10
August ...	— 20	— 3	— 58	— 5	— 22
September.	— 26	— 45	— 14	— 32	— 29
October...	— 52	— 17	— 40	— 45	— 38
November.	— 10	— 18	— 4	— 55	— 22
December.	— 30	— 8	— 17	— 20	— 19
January...	— 9	+ 14	+ 14	+ 1	+ 5
February .	— 2	— 22	+ 51	— 8	+ 5
March	+ 18	+ 6	+ 13	+ 39	+ 19
April	+ 46	+ 13	+ 13	+ 52	+ 31

In each of the 4 partial results the supplementary inequality is quite evident. Its amplitude is of the same order of magnitude as in the period 1877—98. There appears to be no reason for assuming any change in this amplitude during the 12 years 1862—74. I therefore tried to represent the general means by a formula and it appeared that a pretty satisfactory representation may be obtained by a simple sine:

$$\Delta g = + 0^{\text{s}}.0341 \cos 2 \pi \frac{T - \text{Apr. 23}}{365}.$$

The sinusoid corresponding to this formula, together with the points given by the observation is represented in Fig. 4.

The differences between the observation and the curve, in thousandth parts of the second, are as follows:

May + 17	Sept. — 2	Jan. + 9
June — 2	Oct. — 4	Febr. — 8
July + 6	Nov. + 9	March — 8
Aug. — 9	Dec. + 1	April — 3

The fact that the supplementary term can be represented by a simple sinusoid and that a half-yearly inequality is not shown, agrees with the result found a moment ago, that no term varying as the square of the temperature is indicated ¹⁾. Properly speaking the two results are equivalent.

16. Finally I have again tried to clear the monthly means of the rates, as well as possible, of all periodic terms. In doing this I have applied no further corrections for the influence of the temperature because the variation of its coefficient — the results of the years 1871 and 1873 are just those differing most considerably — did not seem as yet sufficiently demonstrated.

No other reductions were applied, therefore, but those for the supplementary term according to the formula found above.

The rates corrected in this way (= term α) have been inserted, in the table already given, in the column Red. D. R. II.

These values of the term α have been represented as well as possible by a simple curve reproduced in Fig. 5.

In this figure the results of the observation are also shown, not for every month separately, but for the mean of any three consecutive months ²⁾.

I have tried to draw this curve about as simply as that for the period 1878—98. The outstanding differences $O-C$ (C = curve) are contained in the last column of the table.

These differences lead to the following mean amounts, which we might consider as the mean errors of a monthly mean :

$$\begin{array}{l} 1862-1867 \text{ M. E. } = \pm 0^s.0309 \\ 1868-1874 \quad \quad \quad .0273 \end{array}$$

¹⁾ The remark made at the end of § 7, p. 23 (90) does not make sufficient allowance for the fact that, as long as no physical explanation has been given for the "supplementary term", a variability of this term might be deemed no more probable than the variability in the course of time of a term varying as the square of the temperature.

²⁾ On page 24 (91) I forgot to remark that the same was done in Fig. 3, which represents the period 1878—1898.

whereas, if we had neglected the consideration of the supplementary term, we should have found :

$$\begin{array}{rcl} 1862-1867 \text{ M. E.} & = & \pm 0^s.0382 \\ 1868-1874 & & .0377 \end{array}$$

which values are considerably greater.

IV. *The period 1899—1902.*

17. Since the time, 1898 December, that the clock Hohwü 17 has been mounted in the niche of the pier of the 10-inch-refractor, its rates are kept under constant control by computations which are made, immediately after the time-determinations, by Mr. HAMERSMA, computer at the observatory. He computes moreover mean values of the rate at the end of every month, which are at once inserted in graphical representations. The following investigation was founded on these results only slightly modified.

The modification is the consequence of a small correction of the barometer-readings caused by the fact that the temperature of the clock is no longer the same as that of the barometer in the transit-room. The barometer-readings were reduced therefore to what they would have been at the former temperature ¹⁾. As my investigation, which includes no more than three years, must be considered as a preliminary one, it seemed useless to replace the original mean readings by the mean values according to the barograph-diagrams. Moreover the constant correction of the barometer used was neglected.

As before the temperatures were determined from the readings of the upper one of the two thermometers suspended in the clock case. The former thermometers had been replaced however by two other ones having centigrade scales.

Besides the temperature in the niche below the clockcase has been determined for the period of a year by means of a thermograph of RICHARD. It appeared that, even there, no trace of a daily period in the temperature is noticeable.

In general the changes in the temperature have now become much slower and much more regular. At the same time the temperature in winter time does not nearly sink to so low a point as formerly ; this is shown even in the monthly means. In the years now under consideration the temperature in the clock case never sunk below $+ 2^{\circ}$ C.

As was done for the other periods, I have computed the differences

¹⁾ The reduction amounted to 0.4 Mm. in maximo.

between the upper and lower thermometer for this period after the clock had been mounted in the niche. The monthly means of these differences, resulting from the five hours of observation and from the three years 1899—1901, are as follows:

January	+ 0.02	July	+ 0.21
February	+ 0.01	August	+ 0.17
March	+ 0.01	September	+ 0.06
April	+ 0.02	October	+ 0.02
May	+ 0.05	November	+ 0.01
June	+ 0.15	December	+ 0.02

The differences are now expressed in degrees Celsius. The index-errors of these thermometers are insensible.

18. The observed daily rates were originally reduced to 760 Mm. and + 10° C. by means of the coefficients:

$$b = + 0^s.0140$$

$$c = - 0.0170$$

In the following table, however, the Red. D. R. I. have been computed, not with this value of the temperature coefficient, which had originally been derived from only the first months, but with the value

$$c = - 0^s.0220$$

which accords better with the observations. The meaning of the two last columns of the table will be explained hereafter.

The four months immediately following the mounting and the regulation of the clock, during which the rate proved to be still somewhat variable, have been left out of consideration and have not been inserted in the table.

	Obsd D. R.	Bar.	Temp.	Redd D. R. I	Redd D. R. II	Redd D. R. III
					— 0.157 ^s	— 0.169 ^s
1899 May	— 0.116 ^s	763.2	+ 11.8	— 0.121 ^s	— 4	+ 6
June	0.132	65.7	15.0	0.102	+ 17	+ 30
July	0.192	65.4	18.1	0.090	+ 42	+ 43
Aug.	0.228	66.0	18.7	0.120	+ 36	+ 31
Sept.	0.353	59.1	16.0	0.208	— 11	— 14

	Obsd D. R.	Bar.	Temp.	Redd D. R. I	Redd D. R. II	Redd D. R. III
					^s — 0.157	^s — 0.169
1899 Oct.	— ^s 0.160	767.0	+ 11.7	— ^s 0.221	+ 1	— 4
Nov.	0.156	67.4	11.6	0.225	— 13	— 6
Dec.	0.048	61.7	5.7	0.167	+ 13	+ 10
1900 Jan.	0.097	59.6	5.7	0.186	— 30	— 29
Febr.	0.158	52.8	5.4	0.158	— 18	— 29
March	0.058	61.1	6.5	0.151	— 22	— 33
April	0.065	62.2	8.4	0.131	— 10	— 13
May	0.153	62.2	11.7	0.147	— 30	— 20
June	0.247	61.7	16.4	0.130	— 11	— 5
July	0.258	63.8	18.3	0.128	+ 4	+ 2
Aug.	0.328	62.8	18.2	0.187	— 31	— 31
Sept.	0.252	67.4	16.5	0.214	— 17	— 23
Oct.	0.278	61.9	13.6	0.226	— 4	— 10
Nov.	0.255	58.4	10.2	0.229	— 17	— 13
Dec.	— 0.129	61.2	8.8	0.172	+ 8	+ 27
1901 Jan.	+ 0.052	63.2	5.2	0.099	+ 57	+ 52
Febr.	+ 0.023	61.1	5.1	0.099	+ 41	+ 27
March	— 0.098	57.7	6.7	0.134	— 5	— 16
April	0.105	59.7	9.6	0.110	+ 11	+ 14
May	0.104	65.1	12.6	0.118	— 1	+ 9
June	0.216	64.3	16.0	0.144	— 25	— 16
July	0.266	64.5	19.3	0.125	+ 7	— 3
Aug.	0.286	65.5	19.2	0.161	— 5	— 15
Sept.	0.315	61.7	16.2	0.203	— 6	— 11
Oct.	0.266	61.7	13.5	0.212	+ 10	+ 3
Nov.	0.120	64.0	9.7	0.183	+ 29	+ 32
Dec.	0.185	56.5	7.3	0.196	— 16	— 6
1902 Jan.	0.070	62.8	7.5	0.163	— 7	+ 8
Febr.	0.034	59.6	4.6	0.147	— 7	— 26
March	0.107	57.9	7.8	0.126	+ 3	+ 1
April	0.085	61.6	10.0	0.107	+ 14	+ 18

19. The reduced daily rates I of this table show at once and with evidence the presence of the supplementary term; for the rest the rate of the clock in the present period appears to be a very regular one. If, first of all, we combine the monthly means into 3 yearly means, from May to April, we find:

1899	— 0. ^s 158
1900	.156
1901	.157

There is no trace of a progressive change in the rate and for the further investigation of the influence of the temperature we may simply use the deviations from the general mean = — 0.^s157.

If in the first place we assume that the influence of the temperature is a linear one, we find

1st from the monthly means,

2nd from the means for two months combined in such a way that the supplementary term is nearly completely eliminated, respectively:

$$c = - 0.^s0224$$

and

$$= - 0.0220$$

which values are practically identical with that used for the determination of the reduced daily rates I.

In the second place let us assume the existence of a term varying as the square of the temperature. In this assumption we find, proceeding in the same way as before, for the total influence of the temperature: ¹⁾

$$- 0.^s0253 (t-10^{\circ}) + 0.^s00074 (t-10^{\circ})^2$$

and

$$- 0.0247 (t-10^{\circ}) + 0.00069 (t-10^{\circ})^2$$

respectively. We thus find for this period a quadratic term of appreciable value. The difference between the two formulae is small; I will definitively adopt the former.

20. It thus becomes necessary to use a quadratic formula in order to clear the rates completely from the direct influence of the temperature, as is required for the determination of the supplementary inequality. We may, however, as well *take* the influence of the temperature *to be proportional to its first power* and then *consider* the remaining periodic part of the rate as “supplementary inequality”.

I have followed both ways. In the following table I have inserted, first, the values found for the supplementary term in the first way, giving the results of the three years separately, as well as in the mean. These mean values are pretty well represented by the following simple sine-formula:

¹⁾ The mean temperature of the 3 years was + 11°.6 C.

$$\Delta g = + 0.80465 \cos 2\pi \frac{T - \text{May } 3}{365}$$

The last column of the table contains the differences between the observation and the computation. Everything has been expressed in thousandth parts of the second.

	1899	1900	1901	Mean	O.—C.
May.....	+ 52	+ 26	+ 55	+ 44	— 2
June.....	+ 65	+ 30	+ 19	+ 38	+ 3
July....	+ 58	+ 17	+ 12	+ 29	+ 14
August.....	+ 22	— 40	— 24	— 14	— 5
September..	— 45	— 54	— 42	— 47	— 16
October.....	— 48	— 54	— 41	— 48	— 4
November...	— 52	— 59	— 14	— 42	+ 4
December...	— 25	— 8	— 41	— 25	+ 10
January....	— 44	+ 37	— 7	— 5	+ 10
February...	— 20	+ 36	— 17	0	— 9
March.....	— 2	+ 15	+ 32	+ 15	— 16
April.....	+ 31	+ 58	+ 62	+ 50	+ 6

The mean monthly results of the observations, together with the sinusoid by which they are represented, have been reproduced in fig. 6.

In the second place we give, in the column *O* of the following table, the values of the supplementary inequality which we find in the mean, if we assume $-0.0220 (t-10^\circ)$ for the influence of the temperature. These values are represented by a curve reproduced in fig. 7. The column *O.—C.* of the table contains the deviations from this curve.

	<i>O.</i>	<i>O.—C.</i>		<i>O.</i>	<i>O.—C.</i>
May	+ 28	— 12	Nov.	— 55	0
June	+ 32	— 6	Dec.	— 21	+ 2
July	+ 43	+ 18	Jan.	+ 8	+ 7
Aug.	+ 1	0	Febr.	+ 22	+ 5
Sept.	— 51	— 11	March	+ 20	— 8
Oct.	— 63	+ 2	April	+ 41	+ 5

As might have been expected, the curve shows clearly a half-yearly inequality.

21. Finally I have reduced the monthly means of the rates both, by the linear temperature formula with the curve of fig. 7, and by the quadratic formula with the sinusoid of fig. 6. The rates, thus reduced, have been inserted in the columns Red. D. R. II and Red. D. R. III of the general table.

These columns do not contain the reduced rates themselves, but their mean values, together with the deviations from the latter.

These deviations lead to a mean error of a monthly mean

$$M. E. = \pm 0^s.0211$$

if we adopt the linear formula (Red. D. R. II), and

$$M. E. = \pm 0^s.0218.$$

if we adopt the quadratic formula (Red. D. R. III).

The two methods of reduction thus lead to nearly the same degree of agreement and a decision about the preference to be given to one of the two cannot, therefore, be derived from the monthly rates.

If no reduction for the supplementary inequality had been applied, we should have found in the two cases :

$$M. E. = \pm 0^s.0422$$

$$" = \pm 0.0398.$$

The increase of the *M. E.* is still considerably greater than it is for the other periods. The quadratic formula now leads to slightly better results than the linear one ; the difference is small, however.

V. *Amplitude of the oscillations of the pendulum in the period 1878—1888.*

22. As has been mentioned before, H. G. VAN DE SANDE BAKHUYZEN caused a small mirror to be attached to the pendulum in 1877¹⁾, for the purpose of determining accurately the amplitude of the oscillation by the aid of the reflected image of a metallic wire placed before a flame of petroleum. The image was projected on a divided scale by means of a lens. 1 Mm. in the scale nearly corresponds to 0.5 in the total amplitude ; the reading could be made accurate to tenths of the millimeter. In this way a determination of the amplitude was made, generally 4 times a day, from 1878 April to 1899.

The determinations of the years 1878, 79 and 80 were elaborately studied by H. G. VAN DE SANDE BAKHUYZEN. The influence of the temperature, of the atmospheric pressure and also that of the position of the driving weight were thoroughly investigated. Having the inten-

¹⁾ See: Verslag van den staat der sterrenwacht te Leiden 1876—77 pag. 12.

tion of prosecuting this investigation he did not yet publish his results.

23. It seemed possible that the investigation of these amplitude-observations might contribute to the discovery of an explanation of the supplementary term found in the rates. I intended therefore to inquire whether the corrected amplitudes too would still show a yearly inequality.

As H. G. VAN DE SANDE BAKHUYZEN gave leave to take advantage of his results for the present paper, his corrected amplitudes could be compared at once with each other for the period 1878—80. Furthermore I tried to execute a somewhat provisional investigation for the eight following years. For these years the monthly means of the amplitude found in a first approximation ¹⁾ were corrected for the influence of the atmospheric-pressure, as found by H. G. VAN DE SANDE BAKHUYZEN. A correction for the temperature was not so easily applied, because it appeared that its influence has considerably increased in the course of the years. Finally I proceeded simply in this way, that I derived the value of the amplitude for $+ 8^{\circ}$ R. for every spring and every autumn by interpolations between monthly means corrected for the barometer-reading.

The results have been brought together in the following table :

	Spring.	Spring red.	Autumn.	A.—S.
1878	37.77	38.22	39.71	$+ 1.49$
1879	38.68	38.76	37.66	$- 1.10$
1880	38.84	40.06	39.50	$- 0.56$
1881	41.27	40.48	40.47	$- 0.01$
1882	39.70	39.18	39.19	$+ 0.01$
1883	38.66	35.42	35.67	$+ 0.25$
1884	32.19	30.70	29.22	$- 1.48$
1885	29.20	30.55	28.35	$- 2.20$
1886	31.90	32.30	32.33	$+ 0.03$
1887	32.71	31.86	31.68	$- 0.18$
1888	31.01			

¹⁾ As many observations are wanting the corresponding values had to be assumed.

These results are expressed in millimeters of the scale and they represent the total amplitude on that scale diminished by 320 Mm.

The 2nd and the 4th column contain the results obtained for the spring and the autumn; the 3rd contains the means of two consecutive results for the spring; the 5th the differences autumn — spring obtained by subtracting the numbers of the 3rd column from those in the 4th. The differences prove to be very small; their mean amounts only to -0.38 Mm. or, if we exclude 1878 on account of a possible displacement of the lens, -0.58 Mm., *i. e.* -0.2 or -0.3 respectively, whereas the effect of 1° R. is 0.6 in the beginning and about $1'$ afterwards. Besides, the sign of the mean difference is the reverse of what we should have found, when the amplitude of the pendulum lags behind the temperature. Thus already this superficial investigation seems to show, that there is no term in the amplitude analogous to the supplementary term in the rates.

VI. *Comparison of the results.*

24. If we consider the results obtained in the preceding pages in their mutual relation, we are struck in the first place by the fact that the clock HONWÜ 17, which at present has been going for more than forty years, far from showing the defects of old age, has increased on the contrary in regularity of rate in the course of the years. We have seen that both in the period 1862—1874 and in that of 1878—1898 the greatest regularity was only reached after some years. It may be pointed out now that this regularity has also increased from period to period.

For we found for the mean deviation of the monthly means from a simple curve (1st and 2nd period) or from a constant value (3rd period) the numbers:

1862—1874	± 0.0291
1879—1896	$.0237$
1899—1902	$.0215$

The diminution of the mean deviation is considerable and whereas in the 3rd period the amelioration in the clock's position may have contributed towards this diminution, the difference between the first and the second is very striking. We have to consider in this connection that, for the two former periods, a whole year at the beginning has been left out of consideration, whereas for the third the 5th month has already been taken into account.

The only point in which the second period is at a disadvantage

as compared to the first is that the influence of the temperature has been more variable.

This however is mainly the case only for the last years, when, evidently, the cleaning of the clock had been already too long deferred.

If we reduce the temperature-coefficient found for the third period to what it becomes for 1° R. instead of for 1° C., if further we reduce the mean coefficient of the first period to the value which would have been found, had not the barometer-reading been reduced to 0° , and if, lastly, we add the value found for the middle part of the second period ¹⁾, leaving the quadratic terms out of consideration throughout, we find:

1862—1874	$c = - 0.0196$
1885—1891	$- 0.0269$
1899—1902	$- 0.0275$

Between the 2nd and the 3rd period the pendulum has not been taken to pieces and only a small stain of rust has been removed from the suspension-spring.

25. Let us now consider the results obtained for the supplementary inequality. Setting aside a half-yearly inequality, sometimes shown, which is connected with the precise form of the influence of the temperature, we find in all the periods a supplementary yearly inequality in the rates which can be nearly represented by a simple sinusoid having its maxima about May 1 and November 1, the semi-amplitude of which amounts to:

1862—1874	$+ 0.0341$
1878—1886	.0455
1887—1896	.0254
1899—1902	.0465

In the latter part of the period 1878—1898 the amplitude of the supplementary inequality seems to have appreciably diminished so that in the years 1897—1898 it is hardly sensible. For the rest the amplitude of the inequality appears to have had nearly the same amount under any circumstances.

The question now arises:

What explanation can be offered of this inequality? If we consider only the monthly rates, we may mathematically represent it as a lagging behind of about half a month of the influence of the temperature. This cannot be the true physical explanation, however,

¹⁾ See also the values of c for the 2nd period on p. 20 (87).

because it appears from the rates during short periods, that abrupt changes in the temperature are reflected almost immediately. Notwithstanding this, I deemed it possible, at first, that the true explanation might be found in such a cause, by assuming that *part* of the effect of the temperature on the rate — perhaps by the intervention of the elasticity of the suspension-spring, — is only felt after a long time. In this case however, we ought to find another and smaller temperature-coefficient from swift changes in temperature than from the comparison of summer- and winter-rates. In reality, however, it seems, that the coefficients obtained in the two ways agree in the main, at least as far as can be judged now, before the completion of a more elaborate investigation by Mr. WEEEDER.

Besides a change in the elasticity of the suspension-spring, lagging behind the yearly change of temperature, has become improbable since we found no trace of it in the amplitudes of the oscillations.

Another possible explanation might be found in the hypothesis that the temperature of the different parts of the pendulum is permanently unequal and that the distribution of temperature varies systematically with the season, in such a way that it is not identical in the spring and the autumn. The influence of a small inequality of the temperature is considerable. For if the temperature of the pendulum-rod changes only by so much as $0^{\circ}.1$ R., whereas that of the mercury remains constant, the daily rate changes by $0^{\circ}.065$.

The differences between the readings of the upper and lower thermometer in the clock-case must throw light on this distribution of the temperature. The information however must be defective 1st. on account of the small accuracy of the thermometers, 2nd because we do not know the relation existing between the temperature of the steel and the mercury of the pendulum and that of the surrounding air. If we consult the mean values of these differences of temperature for the three periods, we see that in the two former the difference: Upper temperature—Lower temperature has been really found $+0^{\circ}.1$ R. greater in April and May than in October and November. This would produce a difference in the rate agreeing in sign with that which is really found. In the 3rd period, however, spring and autumn agree nearly perfectly.

It seems to me still very uncertain, therefore, whether the cause of the phenomenon in question may be found in this distribution of the temperature. The fact that, whereas the clock was in very different circumstances, the inequality of the rate was very nearly constant and also the fact that it seems to have diminished in the second period, seem, even *a priori*, contrary to such a hypothesis.

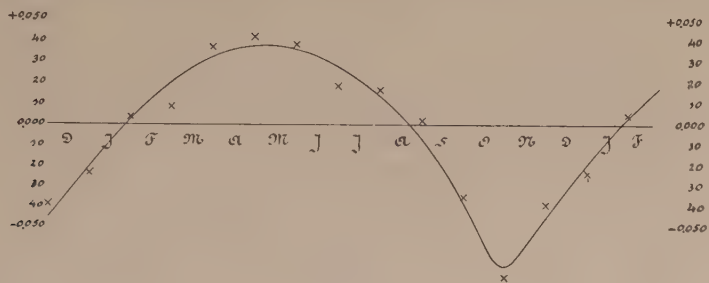


Fig. 1.

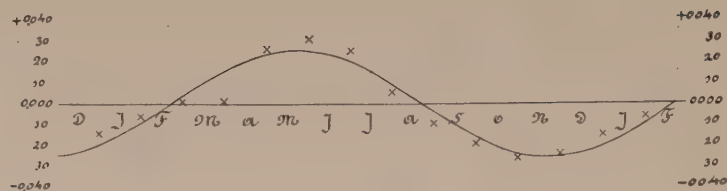


Fig. 2.

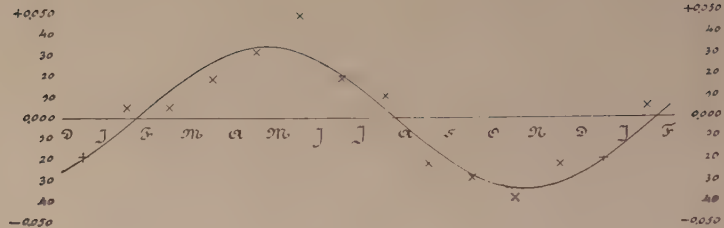


Fig. 4.

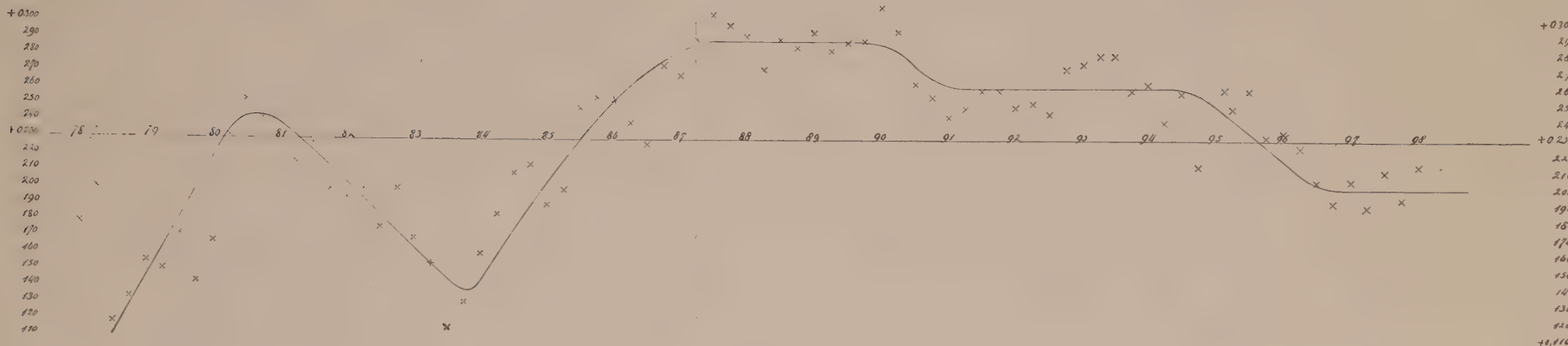


Fig. 3.

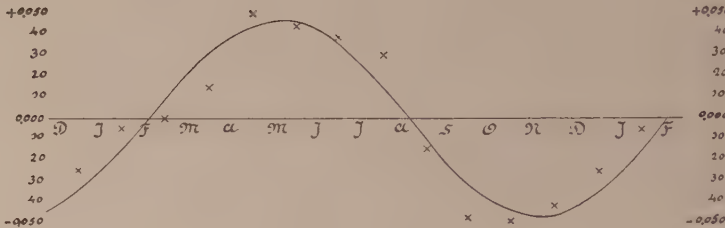


Fig. 6.

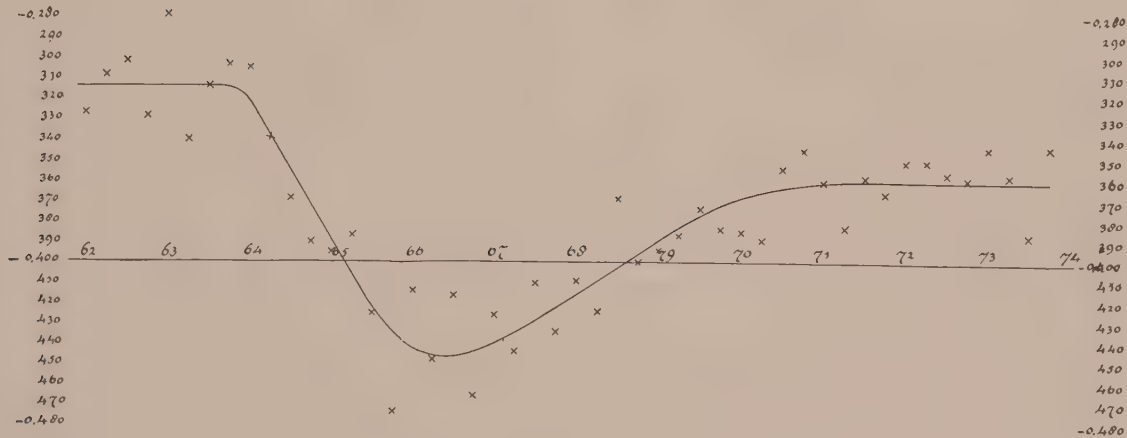


Fig. 5.

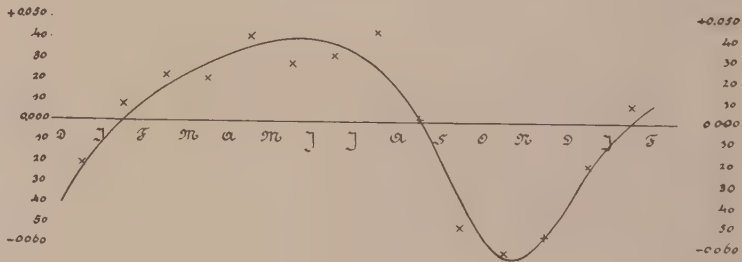


Fig. 7.

And so as yet I feel unable to give a sufficient explanation of the inequality which has been found.

EXPLANATION OF THE FIGURES.

- Fig. 1. Supplementary inequality 1878—1886.
 „ 2. „ „ 1887—1896.
 „ 3. Non-periodic part of the daily rate for $\pm 8^{\circ}.7$ R. 1878—1898.
 „ 4. Supplementary inequality 1862—1874.
 „ 5. Non-periodic part of the daily rate for $\pm 10^{\circ}$ R. 1862—1874.
 „ 6. Supplementary inequality 1899—1902.
 „ 7. The same inequality if the influence of the temperature is assumed to be linear.

In the Fig. 1, 2, 4, 6, 7 the letters D., J. etc. stand for: December 1, January 1, etc.

In the Fig. 3 and 5 the numbers: 78, 62 etc. stand for: 1878 June 15, 1862 June 15 etc.

In Fig. 5 for 79 read 69.

ERRATUM:

p. 47. Behind the title of the communication of Prof. J. W. VAN WIJHE is omitted:

(Communicated in the meeting of April 19, 1902).

(August 8, 1902).

KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN

TE AMSTERDAM.

PROCEEDINGS OF THE MEETING

of Saturday September 27, 1902.

(Translated from: Verslag van de gewone vergadering der Wis- en Natuurkundige Afdeeling van Zaterdag 27 September 1902, Dl. XI).

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The following papers were read:

Physics. — "*On the advantage of metal-etching by means of the electric current*". By Mr. A. H. SIRKS. (Communicated by Prof. J. L. C. SCHROEDER VAN DER KOLK).

(Communicated in the meeting of June 28, 1902).

Side by side with the tension- and bending-tests to which metals and their alloys are submitted, with the object to find out, whether the material answers to the requirements, Prof. BEHRENS gives, as a new method: a microscopic examination, which is deservedly made

use of on a large scale. In a special work on the subject: "Das mikroskopische Gefüge der Metalle und Legierungen," this method and the practical use made of it, is treated exhaustively. The main substance of it is this:

A piece of the material, which is to be submitted to microscopic examination is filed, till it is perfectly smooth, different numbers of carborundum-powder being used for the grinding, after which it is polished with tin-oxide or chrome-oxide, if a perfectly smooth slide is required; then, by means of the annealing colours, the ground plane will show a design, sharp-outlined. Since most metals and alloys have crystal-formations at their fractures, the annealing colours will produce a very strongly marked outline between the crystals and the ground-mass, because it is a known fact, that two substances, submitted to the same temperature, but of different formation (the crystals- and the surrounding mother-water) will not take the same tempering-colours. Next by making scratches on the surface, with needles of known hardness (analogous with the known hardness-scale of Mohs) the hardness of the material may be fixed.

A similar design, not so minutely detailed however, may be called forth by the corroding influence of acids, bases or salt-solutions, which the crystals and the encompassing matter are not equally proof against. For this purpose the rubbing and polishing need not be done so carefully.

This method however has also its difficulties, which may often be very troublesome. As is always the case, when an acid operates upon a metal, also in this etching-process gas will be developed. The microscopically small gas-bubbles which are formed on the slide will locally prevent the corroding process of the acid and be the cause of little holes and dots that have nothing to do with the design and may easily lead to faulty conclusions. The very long time the grinding and polishing sometimes takes (I state here the grinding of different species of iron and babbitts) will keep many from applying this method.

No satisfactory results, in some cases, being obtained by this method, although the material showed distinct crystals at its fracture. Prof. SCHROEDER VAN DER KOLK was struck by the idea, whether it would not be possible to etch metal-planes in another way than by corroding through acids. It is a known fact that a metal in a galvanic cell will corrode at its negative pole. I need only state the equally known fact, that the zinc of a bichromate cell, after the electric current is set working, shows a magnificent structure. To forestall the objection, that the chromic-acid of the cell has been predominating here

in the etching-process, I will just remark that a slight experiment, i. e., by putting the zinc into the fluid, without letting the cell give a current, was sufficient to prove that the etch-design obtained in the first case, stood out in much stronger relief than had been the case, when exclusively applying acids.

As in any electrolytical process anions are formed which together with the metal of the electrode may produce dissoluble salts, it was important to find out what disturbing influence this would have, and combine with it an examination into the practicability of this etching method and see whether it could replace the one of Prof. BEHRENS, in case the results might be unsatisfactory. The corroding influence of acids having to be avoided as much as possible, preference has been given to use the electric current of a battery instead of producing it within the apparatus itself, as happens in any cell. The apparatus was constructed as simply as possible and is exactly the same as that used for ordinary electrolytical experiments.

The object that was to be etched was used as anode (the place where the electric current enters), whereas a piece of copper-plate serves as cathode. The electric current was furnished by an accumulator-battery, having a terminal voltage of 4 volts. In etching alloys of copper, it proved recommendable, every time to connect two apparatuses in series or in some other way to diminish the potential difference, on account of the highly fleecy deposit on the cathode. As electrolyte, water was used to which for every $100 \text{ cm}^3 \pm 6$ drops of diluted sulphuric-acid had been added, in the first place better to conduct the electric current; in the second place, as much as possible, to prevent the formation of base metal-deposits¹⁾. Of course a controlling experiment was taken by hanging a second piece of the alloy, perfectly alike, in a fluid of which the percentage of acid was the same, in order to be able to eliminate etching by the acid. I have preferred to begin experimenting with copper-tin- and copper-zinc-alloys on account of the sometimes beautiful results obtained by the rubbing and polishing method.

In most cases I melted myself the alloys to be sure of the absence of foreign substances, which may cause very great changes in structure.

The metal-slides were hung to a piece of copper-wire, but precautions were taken that there was no contact between the wire and the electrolyte, to be sure that the metal-plate, which had to be etched, did its work as electrode. For half an hour the electrolysis went

¹⁾ In alloys containing lead (babbitts, type-metal, etc.) the sulphuric-acid on account of the indissolubleness of the sulphate of lead was replaced by nitric-acid.

on so as to produce a sharply outlined design on the brass- and bronze-slides.

That to no other cause any difference might be attributed, all slides were finished off in exactly the same way as had been done for the acid-etchings of Prof BEHRENS; the etching standing out much stronger, this soon proved to be entirely superfluous and so the slides were filed only with a smooth-file. The first experiment was taken with a small piece of cast-brass, which proved to be composed of 58.5 % of copper, 40.5 % of zinc, also traces of lead and of tin being found. For half an hour it was submitted to electrolysis, the density of the current being ± 2 amp. p. dM². The result of this experiment is reproduced in fig. 1. The indented structure is very distinctly visible, there being in the slide besides a marked difference in colour between the crystal-formation and the encompassing ground-mass. Bright yellow, the crystals stand out from the enclosing mother-water.

When a second experiment was taken the same alloy was submitted to electrolysis for 12 hours. Under the anode a glass-cup filled with glycerine and with oxide of magnesium was placed to catch up the crystals that might be hollowed out by electrolysis and which will be caused to sink by their weight, for as was to be expected (a thing which was proved by the experiment) the crystals having a higher percentage of copper than the mother-water (in which zinc prevails) will be better proof against electrochemical influence and so in the end get isolated and detached. The residue left in the glass-cup was washed out with alcohol it being found that without this precaution the crystals, that had got detached, easily corroded, leaving nothing behind but a green powder; they were then dried in ether; the residue proved to contain 1.78 mG. metal-crystals. Although these crystals had not got loose entirely intact, they were distinctly angular in form and showed facets. Being submitted to electrolysis (I wish to thank Mr. VERMAES for his assistance in this) these crystals were found to contain 1.19 mG. of copper, equal to a copper-percentage of 66.8%. Traces of lead were found on the anode and proved to be PbO₂, but the quantity was too small to permit weighing.

The second design is of a piece of plate-brass, of which the ground slide is in my possession. Etching and colouring after perfect grinding and polishing, had yielded no result. The result of half an hour's electrolysis with a current of the same density as with the first experiment, and the same fluid as electrolyte, is shown in the adjoined photograph. Also the effect of the mechanic treatment can be distinctly noticed. Everywhere in the slide twin-crystals are to be found, which as Prof. BEHRENS explains in his work, are apt to be formed in conse-

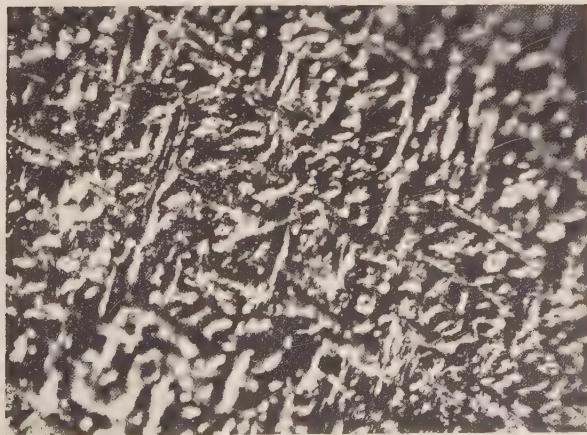


Fig. 1. Cast-brass.



Fig. 2. Platino-brass.



Fig. 3. Bronze for coining.

quence of the mechanic treatment to which the material has been submitted. This slide was the first which was no longer ground with carborundum-powder, but only filed.

The ordinary bronze for coining (see fig. 3) equally shows a structure in which the mechanic operation is visible, both in its crystal-formation and in the position and direction of the crystals, where the more or less flattened parts meet.

From a piece of cast-bronze of a connecting rod a thinnest possible sheet was filed and polished; after heating, stuck on a slide-glass and submitted to etching by electrolysis. A beautifully executed, right-angled lace-work remained, very typical for bronze structures. The encompassing matter of high tin-percentage had been etched away; the crystals, rich in copper, had remained. From a piece of heavily wrought phosphor-bronze, which had remained unaffected by colouring, I have obtained a slide with such a strong relief, that I have not succeeded in taking a photography of it. Also here even the bare eye could see the right-angled structure. The arrangement of the crystals was like that of tiles on a roof.

On account of the great practical use made of white-metal in the technical branches, I have experimented also with that. After half an hour also here, intact cubes of alloy of tin and antimony outlined themselves; also here it was possible to go on etching very deep and without much difficulty to detach the cubes, entirely intact from the alloy. The little time left to me for the moment, necessitates my putting off the analysis of those cubes till later.

Whereas at the beginning only copper-tin and copper-zinc alloys were etched, now also iron has been experimented with. The fact, that it is fine-grained, that the etched facets easily oxidize, that base-metal-deposits¹⁾ are apt to be formed, all that naturally causes difficulties. The use made of salt-solutions, as electrolyte, to diminish the internal resistance, has yielded no result worth mentioning. I have submitted to etching a piece of an iron-bar rolled square. After a few hours the fibrous structure was distinctly visible with the bare eye, both lengthways along the fibres and crosswise, vertically on them. With some difficulty I succeeded in isolating iron-slivers, which, if only collected in sufficient quantity, might be analysed quantitatively. A soele of a gaspipe sawed through, showed cubes in the profile: all the crystals having grouped themselves in the rolling-direction. A piece of a steel angle-iron having been submitted to the bending-test, yielded no other result as

¹⁾ For on account of the corroding influence of acids on iron and steel a very small quantity of sulphuric-acid can be experimented with.

yet, but the one that also here, just as with the piece of bar-iron, the direction of the fibres could be seen with the bare eye, as well as a very distinct difference between the drawn and the compressed fibre.

As to the structure and formation of the carbide crystals nothing could be fixed at this first experiment, I do not doubt however, but also here the results will be satisfactory.

Worth mentioning still is the etching of a cylinder-shaped piece of cast-steel, which was submitted to electrolysis for 36 hours. Although outwardly no etched design could be seen, a porous coat of $\pm \frac{1}{8}$ inch of some iron-carbide appeared to have been formed, which, coming in contact with the air, was apt to oxidize, could be cut with a knife, and in the incision glittered like metal. When analysed the iron-percentage proved to be $91\frac{1}{2}\%$.

The great results, obtained also here, are a stimulus to me, to investigate this matter later more thoroughly.

Those experiments suggested to Prof. SCHROEDER VAN DER KOLK the idea, whether crystals of minerals treated in this way, would show a design. Considering the results, obtained with copper-alloys, a piece of a copper-ore was used for the first experiment. After an hour, also this material showed a distinct etch-design, which is probably connected with a crystal formation. Not to be led away from my subject, I will only just mention the phenomenon.

Before concluding, I will resume the advantages, gained by the way indicated.

1^{stly}. Results having been obtained, where the ordinary grinding-polishing- and etch-methods had failed.

2^{ndly}. The obtained preparations show a far more detailed design, which stands out in much stronger relief than the ordinary etch-slide.

3^{rdly}. It is not necessary to finish off the slides half so carefully, as the tempering-method requires.

4^{thly}. From different alloys crystals or fragmentary crystals have been detached which permit of analysis and show remarkable differences with the average percentage of the alloys.

The good results are a sufficient recommendation for practical purposes, time may still be saved by connecting many apparatuses

in series, so as to be able to etch different slides at the same time.

To my opinion it will be possible with careful treatment (regulating the power of the current and using different acids) in this way, from all cast-metals and alloys, to detach the crystals, thus making it possible to find out the quality and formation of the materials.

After I had concluded these preliminary experiments, it came to my knowledge that the electric current had already been used as an etching medium in the work called "*Contribution à l'étude des Alliages*" edited by the Société d'Encouragement de l'Industrie Nationale, Mr. CHARPY describes a method, successfully made use of by him and which according to the added photograms, shows great resemblance with our method. He namely used an ordinary DANIELL-cell to furnish the electric current and in it replaced zinc by the alloy, that has to be etched, made a short circuit of the cell and obtained an etched design after having submitted the previously polished plane for half an hour to electrolysis.

To my opinion however there are great objections here. For to obtain a somewhat powerful current it is necessary to reduce the inward resistance to a minimum, either by using larger electrodes or by considerably increasing the acid-percentage of the electrolyte. Especially with the etching of iron and steel the high percentage of acid will be an unsurmountable obstacle. A second objection is the impossibility, on account of that acid, to go on etching deep enough to detach crystals, for the angles and ribs which will be laid open by the etching-process will very soon dissolve again.

Before I conclude, I will here openly thank Prof. SCHROEDER VAN DER KOLK for his readiness in furnishing me all I wanted, to render this investigation possible.

The Hague, June 1902.

Physics. — "*On the conditions for the occurrence of a minimum critical temperature for a ternary system.*" By Prof. J. D. VAN DER WAALS.

Already in my "*Molecular theory*" I have derived the condition on which a binary system presents a minimum critical temperature (Cont. II, p. 20). Starting from the form of the equation of state I have assumed there, we namely find:

$$RT_{cr} = \frac{8}{27} \frac{a_x}{b_x}$$

where T_{cr} represents the temperature, for which the maximum and the minimum of the isothermal coincide. Discussing the conditions of coexistence we have pointed out that the critical phenomena for a binary system, though they are different from those which occur for a simple substance, yet in the case that the value of T_{cr} defined by the above equation is a minimum, differ so slightly from those for a simple substance that this equation has a sufficient degree of approximation for the determination of the critical phenomena as we may realize them experimentally. Also for a ternary system the critical phenomena will differ from those for a simple substance, and we may expect that the difference will even be more considerable than in the case of a binary system. Yet also for a ternary system this difference will not be so great, that the conditions for the existence of a minimum value of $\frac{a_{xy}}{b_{xy}}$ will differ sensibly from the conditions for the existence of the minimum critical temperature as it may be realized experimentally.

In order to find this condition for a binary system I have investigated in what circumstances $\frac{a_x}{b_x}$ taken as a function of x , can assume a minimum value, and so I have discussed the equation:

$$\frac{d \frac{a_x}{b_x}}{dx} = 0.$$

Analogous to this we should have to discuss the following equations in order to find this condition for a ternary system:

$$\frac{d \frac{a_{xy}}{b_{xy}}}{dx} = 0,$$

and
$$\frac{d \frac{a_{xy}}{b_{xy}}}{dy} = 0.$$

At present however I will follow another way, which leads us more easily to our aim and which yields the results in such a manner that they may be better surveyed.

If we write for a binary system:

$$\frac{a_1 (1-x)^2 + 2 a_{12} x (1-x) + a_2 x^2}{b_1 (1-x)^2 + 2 b_{12} x (1-x) + b_2 x^2} = \lambda,$$

then the solution of the equation:

$$(a_1 - \lambda b_1) (1-x)^2 + 2 (a_{12} - \lambda b_{12}) x (1-x) + (a_2 - \lambda b_2) x^2 = 0$$

yields that value of x , for which $\frac{a_x}{b_x}$ assumes the given value λ . So we find:

$$\frac{x}{1-x} = -\frac{a_{12}-\lambda b_{12}}{a_2-\lambda b_2} \pm \sqrt{\left\{ \frac{(a_{12}-\lambda b_{12})^2 - (a_1-\lambda b_1)(a_2-\lambda b_2)}{(a_2-\lambda b_2)^2} \right\}}.$$

If:

$$(a_{12}-\lambda b_{12})^2 - (a_1-\lambda b_1)(a_2-\lambda b_2) < 0,$$

the quantity $\frac{x}{1-x}$ is complex. This cannot be the case if the value of λ lies between $\frac{a_1}{b_1}$ and $\frac{a_2}{b_2}$. It can only occur if λ is chosen either smaller than $\frac{a_1}{b_1}$ and $\frac{a_2}{b_2}$ or greater than both these values.

If λ is chosen such that

$$(a_{12}-\lambda b_{12}) - (a_1-\lambda b_1)(a_2-\lambda b_2) = 0 \quad . \quad . \quad . \quad (1)$$

then this equation will yield the minimum value of λ . If we put in this equation either:

$$\lambda = \frac{a_1}{b_1} \text{ or } \lambda = \frac{a_2}{b_2}$$

then the first member will be negative. If we put:

$$\lambda = \frac{a_{12}}{b_{12}}$$

then the sign of the first member will be the same as that of $(a_1 - \lambda b_1)(a_2 - \lambda b_2)$. The second member is positive, if $\frac{a_{12}}{b_{12}}$ is smaller

than $\frac{a_1}{b_1}$ and also smaller than $\frac{a_2}{b_2}$. Consequently a value of λ must

exist for which (1) = 0 and for which therefore $\frac{a_x}{b_x}$ assumes a mini-

mum value. This value lies between $\frac{a_{12}}{b_{12}}$ and $\frac{a_1}{b_1}$; or if $\frac{a_2}{b_2} < \frac{a_1}{b_1}$

between $\frac{a_{12}}{b_{12}}$ and $\frac{a_2}{b_2}$.

In the case that $\frac{a_{12}}{b_{12}}$ is both greater than $\frac{a_1}{b_1}$ and than $\frac{a_2}{b_2}$, the first member of equation (1) changes its sign in the same way, and the value of λ for which the first member vanishes, lies also between $\frac{a_1}{b_1}$ and $\frac{a_{12}}{b_{12}}$ or if $\frac{a_2}{b_2} > \frac{a_1}{b_1}$ between $\frac{a_2}{b_2}$ and $\frac{a_{12}}{b_{12}}$. So for a minimum

value of λ we have $\lambda_m > \frac{a_{12}}{b_{12}}$ and for a maximum value $\lambda_m < \frac{a_{12}}{b_{12}}$.

If λ has the value of λ_m also the following two equations hold:

$$\frac{x}{1-x} = -\frac{a_{12}-\lambda_m b_{12}}{a_2-\lambda_m b_2},$$

and

$$\frac{1-x}{x} = -\frac{a_{12}-\lambda_m b_{12}}{a_1-\lambda_m b_1}.$$

As $\frac{x}{1-x}$ must be positive because x must lie between 0 and 1, the sign of $a_{12}-\lambda_m b_{12}$ is opposite to that of $a_1-\lambda_m b_1$ and $a_2-\lambda_m b_2$. This agrees with what we have deduced concerning the relative value of λ_m and $\frac{a_{12}}{b_{12}}$.

We should have obtained the same results, if we had written the relation $a_x = \lambda b_x$ in the following form:

$$\left\{ \frac{(a_1-\lambda b_1)(1-x) + (a_{12}-\lambda b_{12})x^2}{a_1-\lambda b_1} + x^2 \right\} (a_2-\lambda b_2) - \frac{(a_{12}-\lambda b_{12})^2}{(a_1-\lambda b_1)} = 0.$$

In the case that $a_1-\lambda b_1$ is positive namely this equation cannot be satisfied if the coefficient of x^2 is positive; so if

$$(a_1-\lambda b_1)(a_2-\lambda b_2) - (a_{12}-\lambda b_{12})^2 > 0.$$

If the coefficient of x^2 is zero, then this equation can only be satisfied if we put:

$$(a_1-\lambda b_1)(1-x) + (a_{12}-\lambda b_{12})x = 0.$$

On the other hand in the case that $a_1-\lambda b_1$ is negative this equation cannot be satisfied if the coefficient of x^2 is negative. This however also yields:

$$(a_1-\lambda b_1)(a_2-\lambda b_2) - (a_{12}-\lambda b_{12})^2 > 0.$$

If therefore we have the equation:

$$(a_1-\lambda b_1)(a_2-\lambda b_2) - (a_{12}-\lambda b_{12})^2 > 0$$

then the value of λ must be either less than the minimum value of $\frac{a_x}{b_x}$ or more than the maximum value.

We must however distinguish between a minimum value of λ which occurs at positive value of $\frac{x}{1-x}$ and a minimum value of λ corresponding to a negative value of $\frac{x}{1-x}$. The former, which really

exists, requires that $\frac{a_{12}}{b_{12}}$ is both smaller than $\frac{a_1}{b_1}$ and than $\frac{a_2}{b_2}$. The

latter cannot of course be realized. Solving the equation

$$(a_1 - \lambda b_1)(a_2 - \lambda b_2) - (a_{12} - \lambda b_{12})^2 = 0$$

we find:

$$\lambda = \frac{-(a_1 b_2 + a_2 b_1 - 2a_{12} b_{12}) \pm \sqrt{(a_2 b_1 - a_1 b_2)^2 + 4(a_1 b_{12} - a_{12} b_1)(a_2 b_{12} - b_2 a_{12})}}{2(b_1 b_2 - b_{12}^2)}.$$

This equation can be satisfied by a real value of λ if:

$$\frac{b_1 b_2}{4b_{12}^2} \left(\frac{a_1}{b_1} - \frac{a_2}{b_2} \right)^2 + \left(\frac{a_1}{b_1} - \frac{a_{12}}{b_{12}} \right) \left(\frac{a_2}{b_2} - \frac{a_{12}}{b_{12}} \right) > 0.$$

This equation is certainly satisfied if $\frac{a_{12}}{b_{12}}$ is both smaller than $\frac{a_1}{b_1}$ and than $\frac{a_2}{b_2}$, but it may also be satisfied in other cases. Let us

assume that $\frac{a_1}{b_1} > \frac{a_{12}}{b_{12}}$ and $\frac{a_{12}}{b_{12}} > \frac{a_2}{b_2}$. If we then have:

$$\left(\frac{a_{12}}{b_{12}} - \frac{a_2}{b_2} \right) \left(\frac{a_1}{b_1} - \frac{a_{12}}{b_{12}} \right) < \frac{b_1 b_2}{4b_{12}^2} \left(\frac{a_1}{b_1} - \frac{a_2}{b_2} \right)^2$$

a minimum value of λ occurs indeed, but in this case it corresponds, according to our previous observations, to a negative value of $\frac{x}{1-x}$.

We arrive at the same result starting from the equation of Cont. II p. 20.

For a ternary system we have, putting $\frac{a_{xy}}{b_{xy}} = \lambda$:

$$(a_1 - \lambda b_1)(1 - x - y)^2 + (a_2 - \lambda b_2)x^2 + (a_3 - \lambda b_3)y^2 + 2(a_{12} - \lambda b_{12})x(1 - x - y) + 2(a_{13} - \lambda b_{13})x(1 - x - y) + 2(a_{23} - \lambda b_{23})xy = 0.$$

We may represent this by the sum of three squares:

$$\begin{aligned} & \frac{[(a_1 - \lambda b_1)(1 - x - y) + (a_{12} - \lambda b_{12})x + (a_{13} - \lambda b_{13})y]^2}{(a_1 - \lambda b_1)} + \\ & + \frac{\left[x \left\{ (a_2 - \lambda b_2) - \frac{(a_{12} - \lambda b_{12})^2}{a_1 - \lambda b_1} \right\} + y \left\{ (a_{23} - \lambda b_{23}) - \frac{(a_{12} - \lambda b_{12})(a_{13} - \lambda b_{13})}{a_1 - \lambda b_1} \right\} \right]^2}{(a_2 - \lambda b_2) - \frac{(a_{12} - \lambda b_{12})^2}{a_1 - \lambda b_1}} + \\ & + y^2 \left\{ (a_3 - \lambda b_3) - \frac{(a_{13} - \lambda b_{13})^2}{a_1 - \lambda b_1} - \frac{\left[(a_{23} - \lambda b_{23}) - \frac{(a_{12} - \lambda b_{12})(a_{13} - \lambda b_{13})}{a_1 - \lambda b_1} \right]^2}{(a_2 - \lambda b_2) - \frac{(a_{12} - \lambda b_{12})^2}{a_1 - \lambda b_1}} \right\} = 0. \end{aligned}$$

In the case that $a_1 - \lambda b_1 > 0$ and $(a_1 - \lambda b_1)(a_2 - \lambda b_2) > (a_{12} - \lambda b_{12})^2$, this equation cannot be satisfied if the coefficient of y^2 is positive. If this coefficient decreases to zero, then the equation is satisfied by only one set of values for x and y , namely by those values for

which both the other squares are equal to zero. If the coefficient of y^2 is negative, then a locus exists (a conic section) which indicates all mixtures for which $\lambda = \frac{a_{xy}}{b_{xy}}$ has the same value. If this locus is reduced to one point, as is the case if the coefficient of y^2 vanishes, then λ is for that point a minimum, respectively a maximum. The minimum value of λ satisfies therefore the equation:

$$\{(a_1 - \lambda b_1)(a_2 - \lambda b_2) - (a_{12} - \lambda b_{12})^2\} \{(a_1 - \lambda b_1)(a_3 - \lambda b_3) - (a_{13} - \lambda b_{13})^2\} - \\ - \{(a_1 - \lambda b_1)(a_{23} - \lambda b_{23}) - (a_{12} - \lambda b_{12})(a_{13} - \lambda b_{13})\}^2 = 0,$$

or

$$\begin{vmatrix} a_1 - \lambda b_1 & a_{12} - \lambda b_{12} & a_{13} - \lambda b_{13} \\ a_{12} - \lambda b_{12} & a_2 - \lambda b_2 & a_{23} - \lambda b_{23} \\ a_{13} - \lambda b_{13} & a_{23} - \lambda b_{23} & a_3 - \lambda b_3 \end{vmatrix} = 0. \quad . \quad . \quad . \quad (2)$$

For the determination of x and y we have moreover the equation:

$$(a_1 - \lambda b_1)(1 - x - y) + (a_{12} - \lambda b_{12})x + (a_{13} - \lambda b_{13})y = 0$$

and the equation, which follows from the other square when it is equated to zero.

Another way in which we might have reduced the equation $a_{xy} - \lambda b_{xy} = 0$ to the sum of three squares, would have yielded the following two equations for the determination of x and y .

$$(a_{12} - \lambda b_{12})(1 - x - y) + (a_2 - \lambda b_2)x + (a_{23} - \lambda b_{23})y = 0$$

and

$$(a_{13} - \lambda b_{13})(1 - x - y) + (a_{23} - \lambda b_{23})x + (a_3 - \lambda b_3)y = 0.$$

Eliminating $1 - x - y$, x and y from these three equations in which they occur linearly, we find again equation (2).

In order to calculate x and y we may derive the following relations from these three equations.

$$\begin{array}{c} 1-x-y \\ \hline \begin{vmatrix} a_{12} - \lambda b_{12} & a_{13} - \lambda b_{13} \\ a_2 - \lambda b_2 & a_{23} - \lambda b_{23} \end{vmatrix} \end{array} = \begin{array}{c} x \\ \hline \begin{vmatrix} a_{13} - \lambda b_{13} & a_1 - \lambda b_1 \\ a_{23} - \lambda b_{23} & a_{12} - \lambda b_{12} \end{vmatrix} \end{array} = \begin{array}{c} y \\ \hline \begin{vmatrix} a_1 - \lambda b_1 & a_{12} - \lambda b_{12} \\ a_{12} - \lambda b_{12} & a_2 - \lambda b_2 \end{vmatrix} \end{array}$$

or

$$\begin{array}{c} 1-x-y \\ \hline \begin{vmatrix} a_2 - \lambda b_2 & a_{23} - \lambda b_{23} \\ a_{23} - \lambda b_{23} & a_3 - \lambda b_3 \end{vmatrix} \end{array} = \begin{array}{c} x \\ \hline \begin{vmatrix} a_{23} - \lambda b_{23} & a_{12} - \lambda b_{12} \\ a_3 - \lambda b_3 & a_{13} - \lambda b_{13} \end{vmatrix} \end{array} = \begin{array}{c} y \\ \hline \begin{vmatrix} a_{12} - \lambda b_{12} & a_2 - \lambda b_2 \\ a_{13} - \lambda b_{13} & a_{23} - \lambda b_{23} \end{vmatrix} \end{array}$$

and

$$\begin{array}{c} 1-x-y \\ \hline \begin{vmatrix} a_{23} - \lambda b_{23} & a_3 - \lambda b_3 \\ a_{12} - \lambda b_{12} & a_{13} - \lambda b_{13} \end{vmatrix} \end{array} = \begin{array}{c} x \\ \hline \begin{vmatrix} a_3 - \lambda b_3 & a_{13} - \lambda b_{13} \\ a_{13} - \lambda b_{13} & a_1 - \lambda b_1 \end{vmatrix} \end{array} = \begin{array}{c} y \\ \hline \begin{vmatrix} a_{13} - \lambda b_{13} & a_{23} - \lambda b_{23} \\ a_1 - \lambda b_1 & a_{12} - \lambda b_{12} \end{vmatrix} \end{array}$$

In order that λ have a minimum value for positive values of x , y and $1 - x - y$ the following relations must hold:

$$\begin{aligned}
a_1 - \lambda b_1 &> 0 \\
a_2 - \lambda b_2 &> 0 \\
a_3 - \lambda b_3 &> 0 \\
(a_1 - \lambda b_1)(a_2 - \lambda b_2) - (a_{12} - \lambda b_{12})^2 &> 0 \\
(a_1 - \lambda b_1)(a_3 - \lambda b_3) - (a_{13} - \lambda b_{13})^2 &> 0 \\
(a_2 - \lambda b_2)(a_3 - \lambda b_3) - (a_{23} - \lambda b_{23})^2 &> 0 \\
(a_{12} - \lambda b_{12})(a_{13} - \lambda b_{13}) - (a_1 - \lambda b_1)(a_{23} - \lambda b_{23}) &> 0 \\
(a_{12} - \lambda b_{12})(a_{23} - \lambda b_{23}) - (a_2 - \lambda b_2)(a_{13} - \lambda b_{13}) &> 0 \\
(a_{13} - \lambda b_{13})(a_{23} - \lambda b_{23}) - (a_3 - \lambda b_3)(a_{12} - \lambda b_{12}) &> 0,
\end{aligned}$$

and λ , must satisfy equation (2).

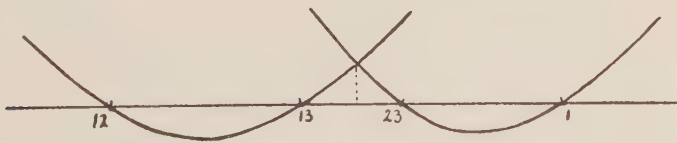
The first set of three inequalities indicates, that this value of λ must be lower than that of the components. The second set indicates that it must be lower than the minimum value of λ for each of the pairs of components of which the ternary system consists. The third set must be fulfilled in order that x , y and $1-x-y$ be positive.

Let us assume $\frac{a_{12}}{b_{12}} < \frac{a_{13}}{b_{13}} < \frac{a_{23}}{b_{23}}$ and suppose that the values of $\frac{a_1}{b_1}$, $\frac{a_2}{b_2}$ and $\frac{a_3}{b_3}$ are higher than that of $\frac{a_{23}}{b_{23}}$ without deciding anything about the relation between the values of the quantities $\frac{a_1}{b_1}$, $\frac{a_2}{b_2}$ and $\frac{a_3}{b_3}$.

According to our assumption the expression

$$(a_{12} - \lambda b_{12})(a_{13} - \lambda b_{13}) - (a_1 - \lambda b_1)(a_{23} - \lambda b_{23})$$

is negative for $\lambda = \frac{a_{12}}{b_{12}}$ and also for $\lambda = \frac{a_{13}}{b_{13}}$ and it is positive for $\lambda = \frac{a_{23}}{b_{23}}$ and for $\lambda = \frac{a_1}{b_1}$. This is perhaps best illustrated by a graphical representation.



Here the points 12 and 13 represent the values of $\frac{a_{12}}{b_{12}}$ and $\frac{a_{13}}{b_{13}}$ and the parabolic curve passing through these points the value of

$$(a_{12} - \lambda b_{12})(a_{13} - \lambda b_{13}).$$

In the same way the points 23 and 1 represent the value of $\frac{a_{23}}{b_{23}}$ and of $\frac{a_1}{b_1}$ and the parabolic curve passing through these points the value of

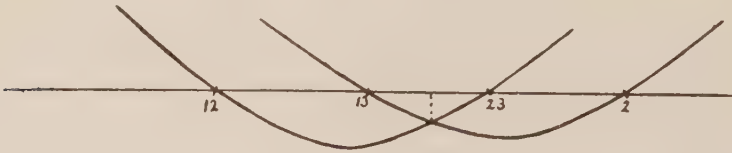
$$(a_1 - \lambda b_1) (a_{23} - \lambda b_{23}).$$

These parabolae intersect between the points 13 and 23 and on the right side of the point of intersection the first mentioned parabola lies higher than the second mentioned; the expression under consideration is there therefore positive.

The graphical representation of the expression

$$(a_{12} - \lambda b_{12}) (a_{23} - \lambda b_{23}) - (a_2 - \lambda b_2) (a_{13} - \lambda b_{13})$$

has the following shape:



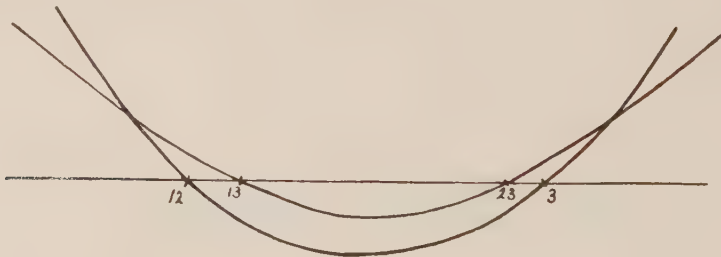
from which we see in the same way that these parabolae intersect between the points 13 and 23 and that this expression is positive for higher values of λ .

The third expression:

$$(a_{13} - \lambda b_{13}) (a_{23} - \lambda b_{23}) - (a_3 - \lambda b_3) (a_{12} - \lambda b_{12})$$

is positive for λ equal to $\frac{a_{12}}{b_{12}}, \frac{a_{13}}{b_{13}}, \frac{a_{23}}{b_{23}}$ and $\frac{a_3}{b_3}$ and, when equated to zero, it will in general not yield a real root; at least not between 12 and 3.

The graphical representation of this third expression has the following form:



where the parabola passing through the points 13 and 23 lies everywhere higher than the other one. The first mentioned parabola would, if there should exist roots, descend below the second one between the points 13 and 23, and so the two roots would lie between those points. But in this case also the third expression is positive above a certain value of λ below $\frac{a_{23}}{b_{23}}$. Or both parabolae might also intersect on the

left side of 12 and on the right side of 1. Also in this case this expression is positive and even within broader limits.

In the case that a value of λ for which the left hand member of equation (2) vanishes, is higher than the value discussed for these three expressions, a minimum value of λ will exist, which represents a really occurring minimum critical temperature. Let us write equation (2) in the following form:

$$\{(a_1 - \lambda b_1)(a_2 - \lambda b_2) - (a_{12} - \lambda b_{12})^2\} \{(a_1 - \lambda b_1)(a_3 - \lambda b_3) - (a_{13} - \lambda b_{13})^2\} - \\ - \{(a_{12} - \lambda b_{12})(a_{13} - \lambda b_{13}) - (a_1 - \lambda b_1)(a_{23} - \lambda b_{23})\}^2 = 0.$$

The first member is negative if we choose for the value of λ either the minimum value of λ for the pair 1 and 2, or for the pair 1 and 3. We will denote these minimum values by $(\lambda_m)_{12}$ and $(\lambda_m)_{13}$.

On the other hand the first member is positive if we choose for λ a value for which the expression, the square of which must be taken, vanishes, — this holds however only in the case that the value of this last root is lower than that of the quantities $(\lambda_m)_{12}$ and $(\lambda_m)_{13}$. In this case the equation (2) has a root which satisfies all the requirements for a minimum value of λ at positive values of $1-x-y$, x and y .

As an instance we choose the following numeric values:

$$b_1=1.6, \quad b_2=1.4, \quad b_3=1, \quad b_{12}=1.5, \quad b_{13}=1.3, \quad b_{23}=1.2 \\ \frac{a_1}{b_1}=3, \quad \frac{a_2}{b_2}=3.2, \quad \frac{a_3}{b_3}=3.372, \quad \frac{a_{12}}{b_{12}}=2.8, \quad \frac{a_{13}}{b_{13}}=2.846, \quad \frac{a_{23}}{b_{23}}=2.9103 \\ a_1=4.8, \quad a_2=4.48, \quad a_3=3.372, \quad a_{12}=4.2, \quad a_{13}=3.7, \quad a_{23}=3.4924$$

From this we find:

$$(\lambda_m)_{12} = 2.933 \dots \dots \dots \\ (\lambda_m)_{13} = 2.962 \dots \dots \dots \\ (\lambda_m)_{23} = 3.15 \dots \dots \dots$$

A value for $\lambda < 2.933 \dots$ makes therefore the three following expressions positive:

$$(a_1 - \lambda b_1)(a_2 - \lambda b_2) - (a_{12} - \lambda b_{12})^2 \\ (a_1 - \lambda b_1)(a_3 - \lambda b_3) - (a_{13} - \lambda b_{13})^2 \\ \text{and} \quad (a_2 - \lambda b_2)(a_3 - \lambda b_3) - (a_{23} - \lambda b_{23})^2$$

For the value of λ for which the quantity:

$$(a_{12} - \lambda b_{12})(a_{13} - \lambda b_{13}) - (a_1 - \lambda b_1)(a_{23} - \lambda b_{23})$$

is positive we find: $\lambda > 2.884 \dots$

For the value for which the expression

$$(a_{23} - \lambda b_{23})(a_{12} - \lambda b_{12}) - (a_2 - \lambda b_2)(a_{31} - \lambda b_{31})$$

is positive we find: $\lambda > 2.855$ and the last of the given expressions

is positive within the limits $\frac{a_{12}}{b_{12}} < \lambda < \frac{a_3}{b_3}$.

The value of λ for which the equation (2) vanishes, lies therefore between 2.884 . . . and 2.933, and the shape of this equation shows that it must lie nearer to 2.933 than to 2.884. We find in fact $\lambda_m = 2.9252 \dots$

With the aid of this value of λ_m we may calculate the values of $\frac{x}{1-x-y}$ and $\frac{y}{1-x-y}$ from the equations of p. 230. But if the degree of approximation with which λ_m is determined is not high, the coordinates of the point to which λ_m relates, are only known inaccurately.

These coordinates however may be calculated directly by means of the following equations:

$$\frac{a_1(1-x-y) + a_{12}x + a_{13}y}{b_1(1-x-y) + b_{12}x + b_{13}y} = \frac{a_{12}(1-x-y) + a_{22}x + a_{23}y}{b_{12}(1-x-y) + b_{22}x + b_{23}y} = \frac{a_{13}(1-x-y) + a_{23}x + a_{33}y}{b_{13}(1-x-y) + b_{23}x + b_{33}y} = \lambda$$

We obtain these equations when we determine the centre of the ellipse

$$a_{xy} = \lambda b_{xy}$$

and when we eliminate the quantity λ from the equations $f'_x = 0$ and $f''_y = 0$. So we find:

$$\begin{aligned} \lambda &= \frac{(a_1 - a_{12})(1-x-y) + (a_{12} - a_2)y + (a_{13} - a_{23})y}{(b_1 - b_{12})(1-x-y) + (b_{12} - b_2)y + (b_{13} - b_{23})y} = \\ &= \frac{(a_1 - a_{13})(1-x-y) + (a_{12} - a_{23})y + (a_{13} - a_3)y}{(b_1 - b_{13})(1-x-y) + (b_{12} - b_{23})y + (b_{13} - b_3)y} \end{aligned}$$

Introducing the condition, that the centre lies on the ellipse itself we get the given equations.

In the case that $b_{12} = \frac{b_1 + b_2}{2}$, $b_{13} = \frac{b_1 + b_3}{2}$ and $b_{23} = \frac{b_2 + b_3}{2}$ which equations may be satisfied approximately, then the locus of the centres is greatly simplified and may be written as follows:

$$\begin{aligned} &\frac{(a_1 - a_{12})(1-x-y) + (a_{12} - a_2)x + (a_{13} - a_{23})y}{b_1 - b_2} = \\ &= \frac{(a_1 - a_{13})(1-x-y) + (a_{12} - a_{23})x + (a_{13} - a_3)y}{b_1 - b_3} \end{aligned}$$

It is therefore a straight line, at least in approximation. With the given numeric values we find:

$$\frac{0,6(1-x-y) - 0,28x + 0,2076y}{0,2} = \frac{1,1(1-x-y) + 0,7076x + 0,328y}{0,6}$$

or

$$0,7 (1-x-y) - 1,5476 x + 0,2948 y = 0.$$

With this simplification the determination of the coordinates comes therefore to the same as the determination of the point of intersection of a conic section, e.g.

$$\frac{a_1(1-x-y)+a_{12}x+a_{13}y}{b_1(1-x-y)+b_{12}x+b_{13}y} = \frac{a_{12}(1-x-y)+a_2x+a_{23}y}{b_{12}(1-x-y)+b_2x+b_{23}y}$$

with a given straight line.

In this case we find:

$$\frac{x}{1-x-y} = \frac{1}{2}$$

and

$$\frac{y}{1-x-y} = \frac{1}{4}.$$

In fact the given numeric values for a_{23} and a_3 were chosen such that we might find simple values for the coordinates.

Because of the asymmetry round the mixture with minimum critical temperature we might of course have expected that the centre of the ellipses which vary with the temperature, would change its place.

For the theory of binary systems it was necessary to introduce the quantity a_{12} , whose value we are not yet able to deduce from the properties of the components. From the calculation of $(\lambda_m)_{12}$ by means of the equation

$$(a_1 - \lambda b_1)(a_2 - \lambda b_2) - (a_{12} - \lambda b_{12})^2 = 0$$

follows, that for substances with a minimum critical temperature this quantity cannot be equal to $\sqrt{a_1 a_2}$ but that it must be less. If it were equal to $\sqrt{a_1 a_2}$ the equation would yield a value $\lambda = 0$.

Moreover it would follow from $a_1 a_2 = a_{12}^2$ that $\frac{a_1}{b_1} \cdot \frac{a_2}{b_2}$ would be greater than $\frac{a_{12}^2}{b_{12}^2}$, as $b_1 b_2$ in any case will be probably less than b_{12}^2 .

For the application of our theory on a ternary system therefore, also knowledge of the quantities a_{12} , a_{13} and a_{23} , is required, which however must be assumed to be known from the knowledge of binary systems.

The theory of the ternary systems therefore does not require any new data, above those of the theory of binary systems.

Physics. — W. H. KEESOM. "*Reduction of observation equations containing more than one measured quantity.*" (Supplement N^o. 4 to the Communications of the Physical Laboratory at Leiden by Prof. H. KAMERLINGH ONNES). .

(Communicated in the meeting of May 31, 1902).

§ 1. The most widely read text books on the theory of probabilities and the method of least squares treat of the reduction of observation-equations each of them containing one variable.

In physical measurements, however, we obtain equations between different quantities each of which must be considered as liable to an accidental error. This, for instance, occurs when we have measured the pressure of a gas or a liquid at different volumes and temperatures, and we want to deduce from the observations the equation which represents the most probable relation between these quantities investigated. As in the literature on this subject I have not found a general solution for such a case, it may be useful to give it here.¹⁾

¹⁾ Literature on this subject:

CHAS. H. KUMMEL. Reduction of observation equations which contain more than one observed quantity. *The Analyst*. July, 1879 (Vol. VI, N^o. 4).

I have not been able to find this volume of the periodical in Holland.

MERRIMAN. The Determination, by the Method of Least Squares, of the relation between two variables, connected by the equation $Y = AX + B$, both variables being liable to errors of observation. U. S. Coast and Geodetic Survey, Report 1890, p. 687. A Textbook on the Method of Least Squares, § 107.

Here an elegant solution of the problem is given for the case in which a linear relation exists between the two measured quantities.

JULES ANDRADE. Sur la Méthode des moindres carrés. C. R. t. 122, p. 1400, 1896.

The author gives a solution for the case when:

$$F(a, b, c \dots; t_i) = N_i,$$

in which t_i and N_i represent measured quantities, and $a, b, c \dots$ are to be determined.

RAVENSHEAR. The use of the Method of Least Squares in Physics. *Nature*, March 21, 1901, p. 489.

The author, apparently not acquainted with the literature mentioned above, points out that in treating equations between several measured quantities, we must make allowance for the fact that each of these quantities has an error of observation, and he gives a graphic solution for the case in which a linear relation exists between two quantities, some supposition regarding the accuracy of the measurements of each of those quantities being assumed.

K. PEARSON. On Lines and Planes of Closest Fit to Systems of Points in Space. *Phil. mag.* (6) Vol. 2, p. 559, Nov. 1901.

The author gives an elaborate essay on the lines and planes (if necessary in a higher-dimensional space) which are such that the sum of the squares of the perpendicular distances between a number of points not situated in a straight line or a plane, and those lines or planes becomes as small as possible.

§ 2. Suppose, we have measured some series of the quantities L, M, N, \dots , between which the following relation exists:

$$F(L, M, N, \dots; X, Y, Z, \dots) = 0 \quad \dots \quad (1)$$

where X, Y, Z, \dots are unknown quantities which we want to calculate. We assume that the number of equations between the observed quantities is larger than the number of unknown quantities, so that we want to calculate the most probable values of X, Y, Z, \dots by means of the method of least squares.

Let L_1, M_1, N_1, \dots be a set of values belonging together, as yielded by the observations,

l_1, m_1, n_1, \dots the errors made in these observations,

$m_{l_1}, m_{m_1}, m_{n_1}, \dots$ the mean errors in those measurements L_1, M_1, N_1, \dots , which we assume to be known before hand,

X_0, Y_0, Z_0, \dots a set of approximate values for X, Y, Z, \dots

x, y, z, \dots the corrections to be calculated, which must be applied to those approximate values.

Each measurement gives then according to (1) an equation:

$$L_1 \cdot l_1 + M_1 \cdot m_1 + N_1 \cdot n_1 \dots = -F_1 - X_1 \cdot x - Y_1 \cdot y - Z_1 \cdot z \dots \equiv \eta_1 \quad (2)$$

where:

$$L_1 = \left(\frac{\partial F}{\partial L} \right)_{\substack{L=L_1, M=M_1 \dots \\ X=X_0, Y=Y_0 \dots}}$$

$$X_1 = \left(\frac{\partial F}{\partial X} \right)_{\substack{L=L_1, M=M_1 \dots \\ X=X_0, Y=Y_0 \dots}}$$

$$F_1 = F(L_1, M_1, N_1, \dots; X_0, Y_0, Z_0, \dots).$$

Yet x, y, z, \dots must be chosen so that¹⁾

$$\Sigma \left(\frac{l_1^2}{m_{l_1}^2} + \frac{m_1^2}{m_{m_1}^2} + \frac{n_1^2}{m_{n_1}^2} + \dots \right) \text{ is a minimum.} \quad \dots \quad (3)$$

If now the coefficients X, Y, Z, \dots , are known, what errors, l_1, m_1, n_1, \dots correspond to the observed quantities L_1, M_1, N_1, \dots ? It is evident that various sets of quantities L, M, N, \dots may have given rise to the same sets of quantities L_1, M_1, N_1, \dots , and that those values of L, M, N and hence of l_1, m_1, n_1 are the most probable for which

$$\frac{l_1^2}{m_{l_1}^2} + \frac{m_1^2}{m_{m_1}^2} + \frac{n_1^2}{m_{n_1}^2} \dots \text{ is a minimum,}$$

¹⁾ KOHLRAUSCH, Lehrbuch der praktischen Physik, p. 16 considers the equations:

$$u = f(A, B, C, r, s, t, \dots)$$

"where r, s, \dots , and often u are instrumental readings" and yet he determines (see p. 11) A, B, C so that the sum of the squares of errors in u is as small as possible.

while we have the relation:

$$\mathbf{L}_1 l_1 + \mathbf{M}_1 m_1 + \mathbf{N}_1 n_1 + \dots = \eta_1 = \text{constant}.$$

We then obtain l_1, m_1, n_1, \dots , from

$$\frac{l_1}{m_{l_1}^2} + K \cdot \mathbf{L}_1 = 0$$

$$\frac{m_1}{m_{m_1}^2} + K \cdot \mathbf{M}_1 = 0$$

$$\frac{n_1}{m_{n_1}^2} + K \cdot \mathbf{N}_1 = 0$$

.....

where:

$$K = - \frac{\eta_1}{\mathbf{L}_1^2 m_{l_1}^2 + \mathbf{M}_1^2 m_{m_1}^2 + \mathbf{N}_1^2 m_{n_1}^2 + \dots}.$$

With this (3) becomes

$$\Sigma \frac{\eta_1^2}{\mathbf{L}_1^2 m_{l_1}^2 + \mathbf{M}_1^2 m_{m_1}^2 + \mathbf{N}_1^2 m_{n_1}^2 + \dots} \text{ is a minimum} \quad (4)$$

If we define the weight of the observation equation by:

$$g_1 = \frac{1}{\mathbf{L}_1^2 m_{l_1}^2 + \mathbf{M}_1^2 m_{m_1}^2 + \mathbf{N}_1^2 m_{n_1}^2 + \dots} \quad (5)$$

then (4) is reduced to

$$\Sigma g_1 \eta_1^2 \text{ is a minimum,}$$

and the equations for the determination of x, y, z, \dots : become:

$$\Sigma g_1 \mathbf{X}_1 \eta_1 = 0$$

$$\Sigma g_1 \mathbf{Y}_1 \eta_1 = 0$$

$$\Sigma g_1 \mathbf{Z}_1 \eta_1 = 0$$

.....

or:

$$\left. \begin{aligned} [g\mathbf{XX}]x + [g\mathbf{XY}]y + [g\mathbf{XZ}]z + \dots + [g\mathbf{XF}] &= 0 \\ [g\mathbf{YX}]x + [g\mathbf{YY}]y + [g\mathbf{YZ}]z + \dots + [g\mathbf{YF}] &= 0 \\ [g\mathbf{ZX}]x + [g\mathbf{ZY}]y + [g\mathbf{ZZ}]z + \dots + [g\mathbf{ZF}] &= 0 \end{aligned} \right\} \quad (6)$$

where, according to the usual notation:

$$[g\mathbf{XX}] = g_1 \mathbf{X}_1^2 + g_2 \mathbf{X}_2^2 + \dots + g_n \mathbf{X}_n^2$$

$$[g\mathbf{XY}] = g_1 \mathbf{X}_1 \mathbf{Y}_1 + g_2 \mathbf{X}_2 \mathbf{Y}_2 + \dots + g_n \mathbf{X}_n \mathbf{Y}_n$$

if n stands for the number of observations.

We hence arrive at this very simple result, that from the equations

$$\mathbf{X}_1 x + \mathbf{Y}_1 y + \mathbf{Z}_1 z + \dots \quad F_1 = 0$$

$$\mathbf{X}_2 x + \mathbf{Y}_2 y + \mathbf{Z}_2 z + \dots \quad F_2 = 0$$

.....

reduced to the linear form, the normal equations are deduced in the same way as when the quantities F_1, F_2, \dots are directly derived

from the observations, if we accord the weight determined by equation (5) to each of those observation equations ¹⁾.

This treatment of the equations with several observed quantities agrees with the solution for two measured quantities given by ANDRADE. For the case that a linear relation exists between two measured quantities this one is simpler than MERRIMAN's solution.

§ 3. In the following way it is easily shown that the mean error in the result is also found according to the usual rules, as applied to equations with one measured quantity. From the normal equations (6) we find

$$x = \alpha_1 F_1 + \alpha_2 F_2 + \alpha_3 F_3 \dots + \alpha_n F_n.$$

Here x is expressed as a function of the measured quantities $L_1, M_1, N_1 \dots L_2, M_2, N_2 \dots$

The mean error in x is obtained from:

¹⁾ For the equations, which SCHALKWIJK used (Comm. Nr. 70, Continued, Proceedings June 1901; Thesis for the Doctorate, p. 115) viz.

$$PV_{20} - 1.07323 = BS_{20}(d - 0.93177) + CS_{20}(d^2 - 0.868),$$

where P and $V_{20} = \frac{1}{d}$ have been measured, BS_{20} and CS_{20} are to be calculated according to the method of least squares, we find from (5) the weight of each observation equation:

$$\frac{g_1}{\mu_0^2} = \frac{1}{P_1^2 V_{120}^2 \mu_{p_1}^2 + \{P_1 V_{120} + BS_{20}d + 2CS_{20}d^{2/3}\} \mu_{d_1}^2}$$

if μ_{p_1} and μ_{d_1} respectively represent the mean relative error in the pressure- and density measurement, and μ_0 the mean relative error for a measurement to which

the weight 1 is assigned. If we put $\mu_{p_1} = \mu_{d_1} = \mu_0 (= \frac{1}{10000})$, then if:

$$d = 6.2394 : g = \frac{1}{2.23},$$

$$d = 53.988 : g = \frac{1}{2.56}.$$

The terms with d will have little influence in the value for g , as long as d does not become very large, as appears a priori from the fact that the coefficients BS_{20} and CS_{20} are small. (Comp. SCHALKWIJK's Thesis for the Doctorate p. 115, where he gives: $BS_{20} = 0.000667^1$, $CS_{20} = 0.00000099^3$). In this case errors of observation in d will have little influence on the second member, and this second member may be considered as precisely known. As the values of PV_{20} differ comparatively little for the different densities at which the observations are made, an equal weight has been assigned to each observation equation. This is the more justified if we consider that he was able to measure the higher pressures with greater precision than the lower, as in the former in adding the measured lengths of each column of mercury the accidental errors partly neutralise each other.

$$m_x^2 = \alpha_1^2 \mathbf{L}_1^2 m_{l_1}^2 + \alpha_1^2 \mathbf{M}_1^2 m_{m_1}^2 + \alpha_1^2 \mathbf{N}_1^2 m_{n_1}^2 + \dots \alpha_2^2 \mathbf{L}_2^2 m_{l_2}^2 + \dots$$

$$\text{or} \quad m_x^2 = \frac{\alpha_1^2}{g_1} + \frac{\alpha_2^2}{g_2} + \dots = \left[\frac{\alpha\alpha}{g} \right].$$

This form is the same as that obtained in equations with one measured quantity ¹⁾, so that here also the weight of the result is found from the coefficients, which occur in the solution for $x, y, z \dots$ if the quantities $[g; \mathbf{X}; F_1]$ etc. in the normal equations are left undetermined.

Mineralogy. — "*On the behaviour of disthene and of sillimanite at high temperature.*" By E. H. M. BEEKMAN. (Communicated by Prof. SCHROEDER VAN DER KOLK).

In nature occur three varieties of aluminium-silicate (Al_2SiO_5) i. e. disthene, andalusite and sillimanite. Sillimanite and andalusite are orthorhombic; disthene however triclinic. So the two first show parallel, the last oblique extinction.

According to the experiments made by VERNADSKY ²⁾, disthene is said to turn into sillimanite, at about 1350 degrees; the same temperature is said to turn also andalusite into sillimanite. As a proof that they had actually become sillimanite, he urged that, whereas before being heated, their hardness and specific gravity differed, they now showed the same. Moreover the extinction of disthene had become parallel.

The results to which he came are these:

Name.	S. G. before heating.	S. G. after heating.
Sillimanite	3.045 3.286	id.
Disthene	3.51 3.48	3.45 3.20
Andalusite	2.85	3.465

Directed by Prof. SCHROEDER VAN DER KOLK, I experimented, as stated by VERNADSKY, and came to the following results, as to their specific gravity:

¹⁾ See for instance MERRIMAN, Method of least Squares, p. p. 83 and 84.

²⁾ See Bulletin de la Société Min. de France (1889 et 1890).

Name.	S. G. before heating	S. G. after heating.
Sillimanite	3.152 3.161	3.157 3.159
Disthene	3.59 3.56	3.240 3.236
Andalusite	3.158 3.158	3.149 3.150

To determine the specific gravity, I made, as much as possible, use of the floating method. The fluids I used were methyl-iodide (spec. gr. 3.51) and acetylenetetrabromide (spec. grav. 2.84). The instrument I used to fix these spec. grav. was the "Westphal-balance", except when the fluids were too light, in which case I made use of a xylolareometer.

Consequently the results, as shown above, are pretty much the same, as those of VERNADSKY.

The extinction of disthene, after the heating, had become parallel also, however before the melting temperature of copper (1100 degr. C.) had been reached.

What is a strong argument against the change of disthene into sillimanite is its index, which I fixed in a way, indicated by Prof. SCHROEDER VAN DER KOLK, i.e. by using fluids of which the refractive index is known¹). They were: methyl-iodide ($n = 1.74$); monobromine-naphthaline ($n = 1.66$); monochlorine-naphthaline ($n = 1.64$); mono-iodine-benzol ($n = 1.62$) and mixtures of them. The index of those fluids, I have fixed by using a Pulfrich with changeable refracting angle.

Thus I could fix the index of very small pieces and moreover acquire a precision up to the second decimal.

I have fixed the index only in the direction of the *c*-axis. The double refraction not being great, this was sufficient. That index is the greatest, since in sillimanite, the ellipse of intersection, with the indicatrix, has its long axis in the direction of the *c*-axis.

Before the heating process, the index of sillimanite was 1.68. Heating did not in the least affect it.

Andalusite remains equally unaffected by it, it has an index of 1.64.

¹) See „Tabellen zur Mikroskopischen Bestimmung der mineralien nach ihrem Brechungsindex" by Dr. J. L. C. SCHROEDER VAN DER KOLK.

The highest temperature to which I have submitted my materials, was acquired by blowing into an open Bunsen flame with an artificial blowpipe-apparatus.¹⁾ The very small splinters of the mineral can be thus brought to a very high temperature probably to 2000° C. A platinum wire of $\frac{1}{8}$ mm. at once melted in it.

As investigation material for disthene, I used the blue variety (find-place Gängerhausen). Before the heating, the index was 1.73 and after it (I experimented in the way just described), it sank to 1.62; so far below that of sillimanite.

If disthene had actually turned into sillimanite, it should have kept its index (1.68); sillimanite submitted to the same temperature, not changing its index in the least. So this shows that heating does not turn disthene into sillimanite.

To try whether 1300° would bring the index to 1.68, I proceeded thus:

I took several earthen mugs, put in each a piece of disthene together with other metals of which the melting temperatures are known, heated the metals to a temperature that would keep them for a moment in melting condition and thus obtaining constant temperatures, I could fix the indices of disthene, which proved to be gradually lower. Lower than 1.62, it could not be reduced, in spite of continued heating. On the subjoined diagram, the different temperatures and indices are stated. On one of the axes are the indices, on the other the degrees from hundred to hundred. The line starting from 1.68, running parallel with the axis of the temperatures, represents the direction of the index of sillimanite. That line remained constant. The broken line marks the direction of the index of disthene. They cut each other, as will be seen, at about 1250° C.

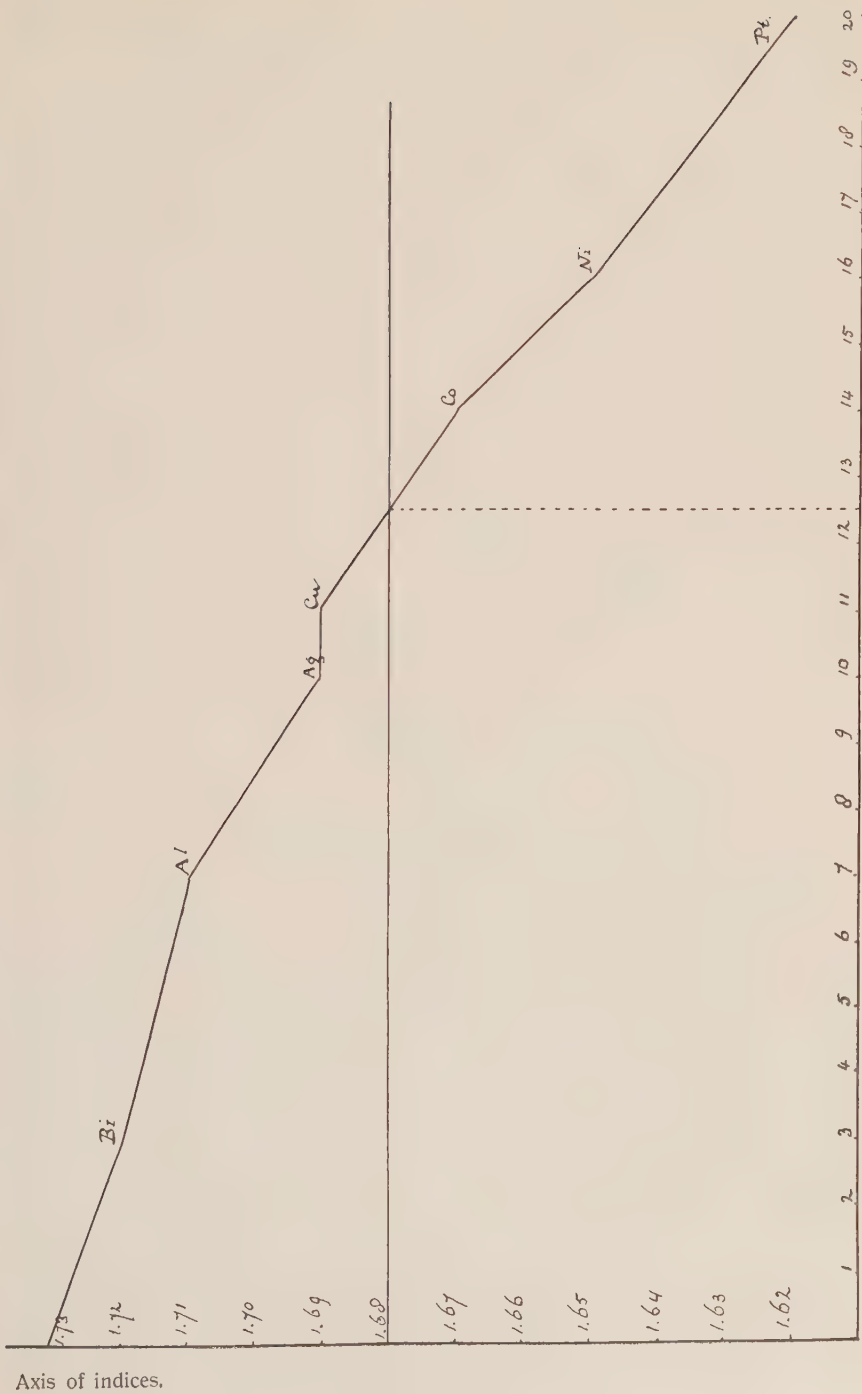
The deviation in silver is probably caused, either by the not absolutely accurate melting temperature or by a slight inaccuracy in the index.

The reason of it is probably that we have a mixture of materials of which one more and more prevails; what pleads for this, is the growing intransparency of disthene, a fact noticed also by VERNADSKY.

At a degree of 1.62 disthene grows entirely opaque, consequently, it has got entirely amalgamated with the other material.

Of course this argument is open to discussion, but up to now, I have not been able to find a better one. This phenomenon, may be of some practical usefulness in making maxim-pyrometers, since it proves that a constant index may be obtained by heating to a certain temperature.

¹⁾ To be had at ALTMANN'S in Berlin.



Physics. — "*Measurements on the magnetic rotation of the plane of polarisation in liquefied gases under atmospheric pressure. II. Measurements with methylechloride*" by Dr. L. H. SIERTSEMA. (Communication n^o. 80 from the Physical Laboratory at Leiden, by Prof. H. KAMERLINGH ONNES).

(Communicated in the meeting of June 28, 1902).

I. In a previous communication n^o. 57 ¹⁾ an apparatus for the measurement of the magnetic rotation in liquefied gases under atmospheric pressure was described and a few results with methyl chloride were given. Further measurements with this apparatus have not fulfilled my expectations, so that it appeared to be necessary to make considerable modifications.

In the first place it was difficult to insulate the apparatus properly from heat. It had been packed in cotton-wool, yet it was not easy to obtain a perfectly quiet liquid, entirely free from rising bubbles. The pressure of as many as six glass-plates between the nicols was also very disturbing, owing to their depolarising influence. This was more noticeable after filling the apparatus when tensions appeared to arise in the plates, in contact with the cold liquid, which often rendered adjustment quite impossible.

To remedy this defect the nicols were immersed in the cold liquid in the tube marked *D* of the plate in the previous communication. The nicols were lying loose in this tube and were connected by a brass wire, running along the outside of the tube. One of the nicols could revolve in its holder and could be adjusted at a given angle before the apparatus was closed. The rotation for different wave-lengths could then be found by measuring the intensity of the current required to bring the dark band in the spectrum to that wave-length. The apparatus being arranged in this manner some measurements could be made with it, but always after some time the nicols appeared to have lost their transparency, either because the layer of canada-balsam was dissolved or became laminated. Nicols with a layer of linseed oil instead of canada-balsam lasted longer, and the layer seems not to dissolve so easily, but in the long run these too lose their transparency, perhaps in consequence of irregular deformation of the calespar by the sudden and intense cold of the liquid gas.

2. Then a new apparatus was constructed, in which also the

¹⁾ Proceedings Royal Acad. of Sciences. May 1900.

first mentioned difficulty was overcome, and with which some satisfactory measurements of the magnetic rotation dispersion in liquid methyl chloride have been made.

In this apparatus, shown in fig. 1, the experimental tube *D* and the nicols *C* are enclosed in a brass jacket *A* with double walls, filled with liquid methyl chloride, insulated from the heat of the coil by a layer of wool. The space within the jacket is closed on either side by the ebonite caps *N* of the previous apparatus, with the india-rubber rings *O* as packing-washers and 6 tightening rods. In these caps the glass plates *B* are fixed with the screw-rings *P*, and thin india-rubber leaf as packing. The other nuts and rings connected with them have remained unchanged.

The circulation of liquid methylchloride through the jacket is obtained from the cryogenic laboratory, where a connection with the methyl chloride reservoir with its compression pump can be made ¹⁾. The liquid is supplied through a high pressure cock *E*, (see fig. 2) while the escaping vapour streams back to the cryogenic laboratory through the tubes *KK*. A float *F* enables us to know at any time whether the jacket is filled.

The experimental tube *D* consists of a glass tube of 35 c.m. having an opening *G* in the middle and closed by two glass plates 1 m.m. thick, fastened to it by means of fish glue. The nicols *C*, rotating in elastic brass rings, are mounted on either side. It is true that now there is glass between the nicols, and the unfavourable influence of this makes itself felt, however to a much smaller extent, so that adjustments can be now made.

The apparatus is filled through a steel capillary *H*, passing through an india rubber stopper in an aperture in the jacket and entering the testing tube.

The methyl chloride required to fill it is obtained by distilling the commercial article, which has been once distilled already, once more, the vapour passing through a drying tube into a spiral immersed in a reservoir of liquid methyl chloride under atmospheric pressure, supplied by the same tubes which were used for the liquid in the jacket described.

Liquid methyl chloride flows from this spiral through the steel capillary *H* connected with it, into the experimental tube under atmospheric pressure and hence having the same temperature as the jacket and the space within. The tube *II* to which a piece of india rubber tubing is connected, serves to remove the vapour formed

¹⁾ Comp. Communication N^o. 14, These Proceedings. Dec. 1894.

inside the jacket. This arrangement proved very satisfactory, the liquid in the testing tube is perfectly quiet and free from bubbles of vapour.

At first the space round the nicols formed one continuous space with that round the testing tube, and so the nicols were also surrounded with an atmosphere of methyl chloride vapour. In consequence of this, vapour still condensed on the nicols and accurate adjustments could not be made. In order to avoid this the spaces round the nicols have been separated from that round the testing tube by the brass rings *L*, fastened on the testing tube by means of sealing wax and closed by means of india rubber rings on the jacket. As at the low temperature a considerable decrease of pressure is to be expected in the imperfectly closed nicol spaces, the caps *N* have been pierced by copper tubes *M*, connected to *U*-tubes with narrow openings and filled with pieces of sodium hydroxide.

Before closing the apparatus, the nicols have been adjusted at a given angle by fastening to one of them a long bent copper-wire, the end of which could be moved over a divided scale. This adjustment is not accurate and no use has been made of this angle in the calculation of the results, the rotations having been compared with those in water.

The rotation at different wave-lengths is again obtained by varying the strength of the current, by doing which, the dark band can be caused to move over the whole spectrum.

The optical and magnetical part is almost the same as that described in the previous communication, except that for the measurement of the current we have again used a d'ARSONVAL-galvanometer with shunt (comp. Comm. Suppl. 1 p. 25, Arch. Néerl. (2) 2 p. 305). By comparing it with a Weston-millivoltmeter it is found that the sensibility of the galvanometer is constant within the limits we had to fix for the accuracy.

Fig. 2 gives a general survey of the apparatus used. *C* represents an arc lamp, *B* ARONS-JUMMER's mercury electric lamp, *A* a collimator, *D* a water reservoir, *P* a prism and *Q* a telescope on a circle from MEYERSTEIN. Further *G* represents the coil with the methyl chloride apparatus, *E* the cock, by which the supply of liquid methyl chloride for the jacket is regulated.

The arrangements for regulating the current and measurement, with resistances and switches, are similar to those for the experiment on the magnetic rotation in gases ¹).

¹) Comm. Leiden Suppl. 1 p. 25; Arch. Néerl. (2) 2 p. 315.

3. For the measurements with methyl chloride of which the results are given below, the nicols were adjusted at an angle of 11 degrees from the crossed position.

The dark band moved from one end of the spectrum to the other as the strength of the current varied from 20 to 60 amp. The observations were made with the electric arc light and the calibration of the spectrum was obtained during the measurements by the brightest mercury lines, while the dispersion curve of the prism had been determined by means of sunlight. At each strength of the current three adjustments of the dark band were made and the means have been taken of the three pairs of readings of the galvanometer and the circle. Table 2 gives the galvanometer defections a so obtained, together with the wave-lengths λ of the position of the dark band in the spectrum.

Then on a subsequent day the testing tube was filled with water and the other parts of the apparatus remounted entirely unchanged. The dark band reappeared at strengths of the current deviating little from those found before, from which we could derive immediately that the rotation constants of liquid methyl chloride differed little from those of water. Thus the numbers of table 1 have been found, where a and λ have the same meaning as they had before, and r stands for the rotation constants in water. The latter have been derived from my measurements of communication n°. 73 ¹⁾, and from them ar has been calculated, which quantity must be constant for all values of r , as it is equal to the rotation angle divided by the magnetic potential difference at the ends of the testing tube, and by the reduction factor of the galvanometer with its shunt.

TABLE 1.

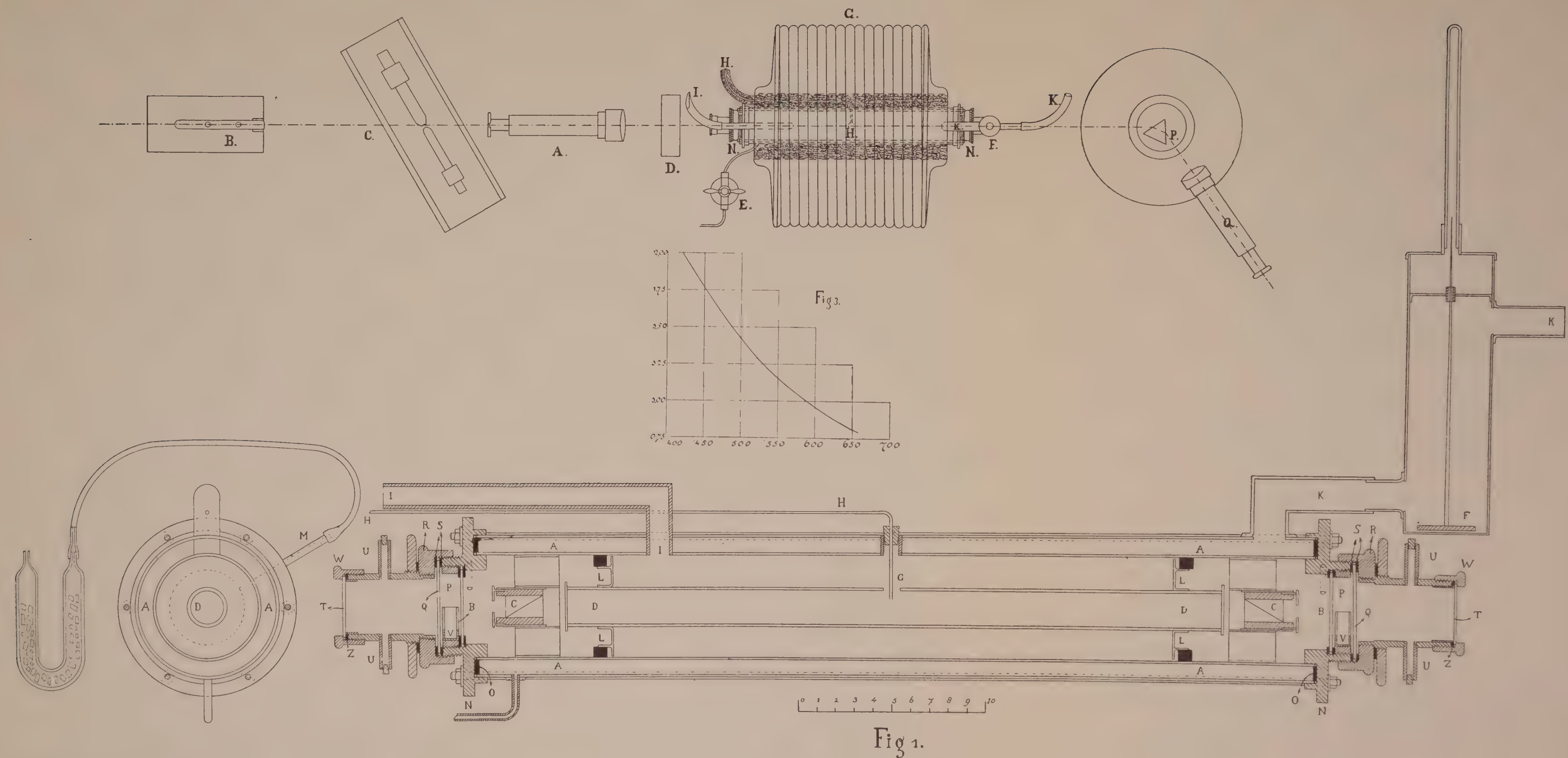
a	λ	r	ar
235	588	0.01307	3.071
490	534	4612	3.062
208.5	554	1487	3.100

mean 3.078

The mean value of ar , being 3.078, now served to derive the rotation constants q of the methyl chloride from the a found. These values of q have been plotted in a curve, from which $q_D = 0.01372$

¹⁾ Arch. Néerl. (2) 6 p. 825 (1901).

Fig. 2.



is derived and the values q/q_D have been calculated finally, which values determine the dispersion of the magnetic gases. These different numbers are combined in table 2, while fig. 3 shows graphically the values of q/q_D .

TABLE 2.

a	λ	q	q/q_D	a	λ	q	q/q_D
112	420	0.02748	2.003	211.5	575	0.01455	1.061
116	431	2653	1.835	216	579	1425	1.039
124	446	2482	1.810	219.5	583	1402	1.022
130.5	458	2358	1.719		[589]	[1372]	1.000
165	510	1865	1.360	231	599	1332	0.971
166	512	1854	1.351	235.5	604	1307	0.953
176.5	527	1744	1.271	237	604	1299	0.947
184.5	536	1668	1.216	249.5	616	1234	0.899
189.5	543	1624	1.184	250	621	1231	0.898
196.5	554	1566	1.142	273	643	1127	0.822
196	555	1570	1.145	283	659	1089	0.794

In this calculation the rotation in the glass plates has been neglected. A simple calculation shows us that this is permissible; for it should be remembered that this is done both for the measurements with methyl chloride and with water.

As the result of this research I find that the magnetic rotation constant for liquid methyl chloride under atmospheric pressure for sodium light is 0.01372, and that the rotation dispersion is normal, deviating little from that with gases and with water.

The research will be continued with other gases.

Physics. — "*Diffraction of Röntgen-Rays.*" By Prof. H. HAGA and Dr. C. H. WIND; second communication.

In the March meeting 1899 we stated as the result of our experiments that Röntgen-rays show diffraction; with these experiments the rays passing through a narrow slit first fell on a second wedge-shaped slit, then on a photographic plate. The image proved not

to be what was to be expected with rectilinear propagation but presented broadenings from which an estimation could be derived concerning the value of the wave-length which proved to be of the order of $0,1 \mu\mu$.

In September of last year in one of the meetings of the "Deutsche Naturforscher Versammlung" at Hamburg Dr. WALTER¹⁾ protested against those experiments; he had arranged his experiments in entirely the same way as we had; moreover he had taken still greater precautions to get a steady mounting of the slits and the photographic plate and he had used stronger Röntgen-rays. WALTER obtained images quite similar to the second slit and attributed our broadenings to inaccuracies of the photographic plate brought about by long development.

These negative results gave rise to a renewed investigation on our side, now that we had greater means at our service than three years ago. We have succeeded in obtaining more clearly than before phenomena of diffraction, so that according to us one can no more doubt the character of Röntgen-rays to be that of disturbances in the ether.

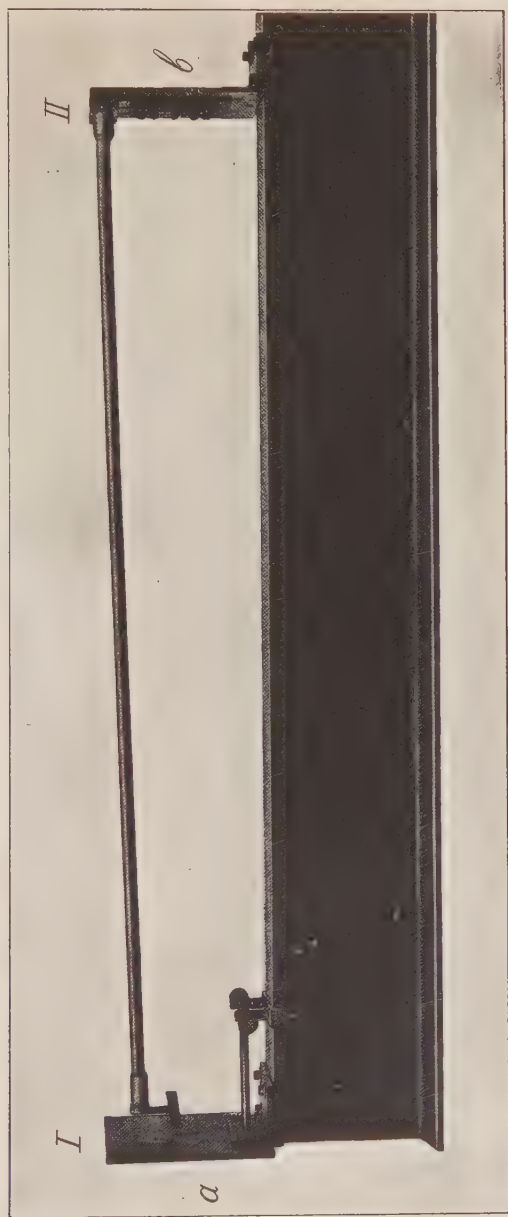
The method of investigation has not changed in principle, but making use of the experience obtained by Dr. WALTER and ourselves we have been able to make improvements still in some respects.

On the upper surface width 5.5 cm. of an iron beam of I-shaped profile, long 2 m. and high 12.5 cm. three pieces of angle-iron were screwed down, one at the end, the two others 75 cm. and 150 cm. distant from it, the edge perpendicular on the length of the beam and the side of 3.5 cm. erect; in the figure the two first pieces of angle-iron are visible; against the vertical sides brass plates — 12 cm. high, 10 cm. wide and 4 mm. thick — were screwed. In the middle of plate I was the first slit, in the middle of plate II the wedge-shaped diffraction slit while against the third plate in a black envelope the photographic plate was clamped²⁾. During the experiments the second and the third of these brass plates were enclosed in an oblong leaden case, which had to prevent the secondary Röntgen-rays or rays diffused by the air, from affecting the photographic plate and causing a fog.

The iron beam was fastened by means of plaster of Paris on two free-stone plates borne by free-stone columns; the columns were placed on a firm pillar; on this same pillar, likewise on a free-stone plate borne by a stone column, was the Röntgen-tube in a large leaden

1) B. WALTER, *Physik. Zeitschrift* 3. p. 137, 1902.

2) SCHLEUSSNER'S "Röntgenplatten" were used.



case (thickness of the side 2 mm.); only the back of this case was left open for the connecting wires of the induction coil, whilst in the front a small aperture was made opposite the first slit to let the Röntgen-rays pass. The first slit was formed by two platina plates, thick 2 mm. and high 2 cm.; a leaden screen left but the middle of it free over a height of 4 mm.; the width of this slit was 15μ . The diffraction slit was formed by two platina plates thick $\frac{1}{2}$ mm., high 4 cm., tapering at the upper end from a width of 25μ to nearly zero at the other. Greatest care was given to the grinding of the platina plates. For these slits, just as in our former experiments, the sides were everywhere equally thick and not ground wedge-shaped at the edge of the slit as is the case with slits for light-experiments.

To produce the Röntgen-rays an induction coil of SIEMENS and HALSKE was used with a sparklength of 60 cm., a primary with 4 coils and a WEHNELT-interruptor. The current was furnished by a battery of accumulators of 110 Volt. The newest Röntgen-tubes of MÜLLER (Hamburg), were exclusively used; the anticathode being kept cool by water.

More care than formerly was taken to bring the passages of the two slits accurately into the same line. Peculiar difficulties are incident to this, which is a result of the extraordinarily great depth of the slits together with a width so slight that common light, on account of the arising phenomena of diffraction, cannot be used to fix accurately the direction of the passage. For this last reason we had to have recourse to Röntgen-rays to do so. And here again the slight width of the slits caused the pencils of rays passing through them to be so very faint, that in the case of the *first* slit, wide 15μ , they could be observed on a fluorescent screen at the place where it was necessary, namely near the second slit only with an eye accustomed to complete darkness. The pencil of rays, allowed to pass through the most interesting part of the *second* slit viz. that part, where the width was about 5μ , could be observed not even by this way, but only by the impression it made on a sensitive plate after a lengthy exposure (4 hours). In order to deduce from this impression a mark for the direction of the passage of the second slit, a small strip of brass was fastened near and slightly above the first slit; (see figure); in this strip, held by an arm fixed to plate II, some vertical rows of small holes had been drilled side by side, differing in number and size. A Röntgen-tube was placed behind plate II in *b* and a photographic plate between the brass strip and plate I; a small leaden screen left of the second slit but the part to be observed free. On the photographic impression one or two of the rows of the holes became visible and from this

could be deduced without difficulty, which part of the strip was situated in the direction of the passage of the second slit. It was now easy to place plate II with its piece of angle-iron in such a way — the holes in the iron were somewhat larger than the diameter of the screws — that, seen from the centre of the second slit, the part of the strip, just now determined, appeared exactly above the first slit. Plate I being able to revolve round an axis through the first slit, the latter could be directed in such a way that the rays from a Röntgen-tube placed near a fell on the second slit; by means of a fluorescent screen we could make sure that this had been obtained. During the course of the diffraction experiments itself the exact position of the tube was several times controlled and if necessary corrected.

The width of the second and first slits were arrived at from photographs when the photographic plate was placed immediately behind plate II and the Röntgen-tube at a or the photographic plate at a against plate I and the Röntgen-tube at b ; the photograph of the second slit was taken both before (namely April 10th, plate N^o. 1) as after (namely Aug. 23rd, plate N^o. 2) the experiments.

As has been mentioned before the self-regulating tubes with water-cooling were exclusively used; how well these tubes work and how excellent they are for the usual medical purposes, for the uncommon demands of this investigation only a few of them could be of service. For we wanted tubes which were "soft" and remained so for hours at a stretch, whilst the effect was so great that the cooling-water kept on boiling; most of the tubes became harder after a ten hours' use; when the discharges took place to the sides of the leaden case another tube had to be taken.

Three very good photographs were obtained, to be distinguished as *A*, *B* and *C*.

A, obtained on May 7th and 8th after an exposure of 9 hours and a half, principally by a very excellent tube furnishing very strong rays and of great softness; developed during three quarters of an hour in 200 ccm. of glycine ¹⁾ 1 to 5.

B, obtained on July 8th, 9th, 10th, 12th; time of exposure 31 hours; two tubes were used, one of which was soft for four hours and after that became hard and the second continually hard; developed in one quarter of an hour with glycine 1 to 5.

¹⁾ VOGEL's Taschenbuch, 1901, pg. 128.

C, Aug. 14th, 15th, 16th, 17th, 18th; time of exposure 40 hours; two tubes used, one of which worked 10 hours and was pretty hard, the other a very good tube which remained soft for the remainder of the time; developed in 10 minutes with glycine 1 to 6.

There is scarcely any fog on the plates.

In order to enquire how wide that part of the diffraction slit was, through which the rays have passed that have worked upon the photographic plate at a definite point, small round holes were drilled just as in our preceding investigation in one of the sides of the second slit and close to it at the extreme ends and in the centre. On account of this on the plates N^o. 1 and N^o. 2 serving for the measurement of the second slit, circular images had appeared and elongated ones on the plates *A*, *B* and *C*. (From these pinhole-photographs of the active part of the anticathode, limited by the width of the first slit, is proved that this active part was only 2 mm. high). The distances between the centres of these images were divided by the dividing-machine into the same number of equal parts, so that the corresponding division-marks point to corresponding places of slit and image.

For the measurement of N^o. 1 and N^o. 2 object-glass *D* and measuring-eye-piece 2 were used where one division of the micrometer corresponds to 3,6 μ .

For the measurement of the image of the slit on *A*, *B* and *C* the microplanar I^a, 2 was used as object-glass and as eye-piece the compensation eye-piece 6; one division of the eye-piece-micrometer corresponds to 55 μ , the magnifying power was 27 with a distance of the image of 25 cm.

In the following table are mentioned for the successive division-marks indicated by their number in the first column:

in column 2: the mean of the values derived from N^o. 1 and N^o. 2 of the width of the second slit in micra;

in column 3: the double width of the second slit augmented by the width of the first slit (15 μ), thus the theoretic width of the image, without diffraction; the distance between the photographic plate and the first slit being double the distance between the first and second slit;

in column 4, 5 and 6: the width of the images respectively on *A*, *B* and *C* as measured in divisions of the eye-piece-micrometer (1 div. = 55 μ);

in column 7: the mean width of the images in micra (rounded off).

Number of the division- mark.	Width of the second slit.	Theor. width of image without diffraction.	Measured width.			
			A.	B.	C.	Mean.
1	27 μ .	69 μ	1.0	1.0	1.0	55 μ
2	22,5	60	0.85	0.85	0.9	50
3	19,5	54	0.75	0.75	0.8	40
4	18	51	0.6	0.7	0.7	40
5	17	49	0.55	0.7	0.7	35
6	16	47	0.45	0.65	0.65	30
7	14	43	0.4	0.6	0.65	30
8	12	39	0.35	0.5	0.6	25
9	9,5	34	0.3	0.4	0.6	25
10	8	31	0.3	0.35	0.5	20
11	6	27	0.4	0.4	0.55	
11 $\frac{1}{2}$			0.6	0.45	0.6	
12	4	23	1	0.45	0.7	
12 $\frac{1}{2}$			$\pm 1\frac{1}{2}$	0.8	$\pm 1\frac{1}{2}$	
13	3.5	22		$\pm 1\frac{1}{2}$		

When considering these figures we must keep in view that the image on account of the width of the first slit is not sharply outlined but is hazy; this causes the measurement to remain uncertain and so somewhat deviating figures are found by different observers or by the same observer at various times; all measurements, however taken, proved, as can be noticed from the figures mentioned in the table, that for the *wide* part of the slit the figures of the third column are larger than the corresponding ones of the last column. The figures of this third column indicate the theoretic width of the image for the case that the plates have been affected to the *outer* edge of the rays to which they were exposed and that no diffraction, vibration, displacement or photographic irradiation has played a part; the latter three causes might bring about a broadening, yet this would necessarily have been greatest on the places of greatest influence thus at the *wide* part of the slit. Now that no broadening whatever is found *there*, the brush-shaped broadenings, whose width is 2 or 3 times greater than the theoretic, found on all the three plates at the narrow part of the slit, can certainly not be attributed to those three causes.

These broadenings, however, are exactly of a character as is to be expected in the case of diffraction; and therefore as long as another explanation is wanting, we can but consider our three plates as so many proofs of *diffraction of the Röntgen-rays*.

Of the most important parts of N^o. 1, *A*, *B* and *C* we have made enlarged copies on glass by means of the microplanar, on which, if not so clearly as under the microscope, the broadening of the image of the slit is yet very distinct; the difficulty of reproducing these enlargements well has made us refrain from publishing them; we are quite willing to send these copies to those who are interested in them.

As to the question to estimate the wave-lengths of these rays, various ways are open; but in no case can one attain at anything but a very rough estimation, as on one hand the real nature of the kind of radiation dealt with is unknown, so that it is uncertain with which kind of diffraction-image our images must be compared, and on the other hand it is very difficult to find out what is accurately the physical meaning of the limits of the image, on which is pointed when measuring.

If however we are forced to limit ourselves to a very rough estimation it is rather indifferent, as far as the result goes, which of the ways already indicated ¹⁾ we take; the simplest method deserves recommendation, namely the one we followed in our first communication about this subject, based upon our estimating the tabular width v of the slit equal to 1.3 at the place where the broadening begins to make its appearance in the image. With a radiation of simple periodical disturbances this tabular width is connected with the wavelength and the linear width, and with the known distances a and b by means of the relation:

$$v_s = s \sqrt{\frac{2(a+b)}{ab\lambda}} \text{ or } \lambda = \frac{s^2}{v_s^2} \frac{2(a+b)}{ab}.$$

As in the experiments a and b both amounted to 75 cm. we obtain after substitution of the value of v_s

$$\lambda = 0,032 s^2.$$

From the above table ensues for s : the width of the slit where the broadening begins to appear, respectively about 7, 4 and 6 μ for the plates *A*, *B* and *C*. From this would ensue for the

¹⁾ H. HAGA and C. H. WIND. These reports 7 page 500, 1899. C. H. WIND Wied. Ann. 68, page 896 and 69, page 327, 1899; Physik. Zeitschrift 2. p. 189, 265 and 292, 1901. A. SOMMERFELD, Physik. Zeitschrift 1, pg. 105, 1900 and 2, pg. 58, 1900; Zeitschrift. f. Math. und Physik. 46, pg. 11, 1901.

wave-lengths if Röntgen-rays are simple periodical disturbances :

for plate	$A,$	$B,$	$C,$
	$\lambda = 0,16$	$0,05$	$0,12 \mu\mu.$

Now that this supposition does certainly not hold, we shall have to consider these values as estimations of wave-lengths, which in the three different experiments have been more or less prominent in the curve of energy ¹⁾ of the Röntgen-rays.

Mention ought to be made here, that, although not too much importance must be attached to the three values of λ as far as the absolute figures go, the difference they show is probably real and connected with the difference in hardness of the tubes. As was mentioned above the tubes used for plate B were distinguished by a considerable hardness from the others, which were relatively very soft.

Worth noticing is also the fact, that the values of λ found here are of the same order as those deduced from our former experiments.

Finally we wish to state emphatically that we continue to regard as the chief result of our investigations the proof they furnish that the Röntgen-rays ought to be considered as a phenomenon of radiation in the ether.

Physical Laboratory University Groningen.

Physics. — H. A. LORENTZ. "*The fundamental equations for electromagnetic phenomena in ponderable bodies, deduced from the theory of electrons.*"

§ 1. In framing a theory that seeks to explain all electromagnetic phenomena, in so far as they do not take place in free aether, by means of small charged particles, electrons, we have to start from two kinds of equations, one relating to the changes of state in the aether, the other determining the forces exerted by this medium on the electrons. To these formulae we have to add properly chosen assumptions concerning the electrons existing in dielectrics, conductors and magnetizable substances, and the forces with which the ponderable particles act on the electrons in these several cases.

In former applications of the theory I have restricted myself to

¹⁾ C. H. WIND. II. cc.

$$\mathfrak{s} = \dot{\mathfrak{d}} + \mathfrak{q} \mathfrak{r}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$Rot \mathfrak{h} = 4 \pi \mathfrak{s}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (III)$$

$$- 4 \pi V^2 Rot \mathfrak{d} = \dot{\mathfrak{h}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (IV)$$

$$Div \mathfrak{h} = 0, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (V)$$

and the electric force \mathfrak{f} , i. e. the force acting on the charged matter per unit charge, will be given by

$$\mathfrak{f} = 4 \pi V^2 \mathfrak{d} + [\mathfrak{v} . \mathfrak{h}] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (VI)$$

§ 3. If it were possible, by means of our observations, to penetrate into the molecular structure of a ponderable body, containing an immense number of charged particles, we should perceive within and between these an electromagnetic field, changing very rapidly and in most cases very irregularly from one point to another. This is the field to which the equations (I)—(V) must be applied, but it is not the field our observations reveal to us. Indeed, all observed phenomena depend on the mean state of things in spaces containing a very large number of particles; the proper mathematical expressions for such phenomena will therefore not contain the quantities themselves appearing in the formulae (I)—(V) but only their mean values. Of course, the dimensions of the space for which these values are to be taken, though very large as compared with the mutual distance of neighbouring particles, must at the same time be very much smaller than the distance over which one must travel in the body in order to observe a perceptible change in its state. We may express this by saying that the dimensions must be *physically infinitely small*.

Let P be any point in the body and σ a physically infinitely small closed surface of which it is the centre. Then we shall define the mean value at the point P of a scalar or vectorial quantity A by the equation

$$\overline{A} = \frac{1}{S} \int_S A d\tau, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

in which the integration has to be extended to all elements $d\tau$ of the space S , enclosed by σ . It is to be understood that, if we wish to calculate the mean value for different points P , P' , the corresponding spaces S , S' are taken equal, of the same form and in the same position relatively to P , P' . The result \overline{A} will depend on the coordinates of the point considered; however, the above mentioned rapid changes will have disappeared from it; it is only the slow changes from point to point, corresponding to the perceptible changes in the state of the body, that will have been preserved in the mean value.

It is easily seen that

$$\frac{\partial \bar{A}}{\partial v} = \frac{\partial \bar{A}}{\partial x}, \text{ etc.}, \quad \frac{\partial \bar{A}}{\partial t} = \frac{\partial \bar{A}}{\partial t}.$$

Hence, if we take the mean values of every term in the equations (I)—(V) and (1), as we shall soon do, we may replace $\dot{\mathbf{d}}$ and $\dot{\mathbf{h}}$ by $\frac{\dot{\mathbf{d}}}{\mathbf{d}}$ and $\frac{\dot{\mathbf{h}}}{\mathbf{h}}$, $\overline{Div \mathbf{d}}$ by $Div \bar{\mathbf{d}}$, etc.

§ 4. Before proceeding further, it is necessary to enter into some details concerning the charged particles we must suppose to exist in ponderable bodies.

Each of these particles calls forth in the surrounding aether a field, determined by the amount, the distribution and the motion of its charges, and it may be shown that, if x, y, z are the coordinates relatively to an origin O taken somewhere within the particle, and if the integrations are extended to the space occupied by it, the field, at distances that are large as compared with the dimensions of the particle, is determined by the values of the expressions

$$\int Q d\tau, \dots \dots \dots (3)$$

$$\int Q x d\tau, \quad \int Q y d\tau, \quad \int Q z d\tau, \dots \dots \dots (4)$$

$$\int Q v_x d\tau, \quad \int Q v_y d\tau, \quad \int Q v_z d\tau, \dots \dots \dots (5)$$

$$\int Q v_x x d\tau, \quad \int Q v_x y d\tau, \quad \int Q v_x z d\tau, \text{ etc.}, \dots \dots (6)$$

Now, we might conceive particles of such a nature that for each of them all these quantities had to be taken into consideration. For the sake of clearness, it will however be preferable to distinguish between different kinds of particles, the action of each of these kinds depending only on some of the integrals (3)—(6).

a. If the charge of a particle has the same algebraic sign in all its points, the actions corresponding to the integrals (3) and (5) will far surpass those that are due to (4) and (6); we may then leave out of consideration these latter integrals. Such particles, whose field is determined by their charge and their motion as a whole, may be called *conduction-electrons*. We shall imagine them to be crowded together at the surface of a charged conductor and to constitute by their motion the currents that may be generated in metallic wires.

b. In the second place, we shall consider particles having in one part of their volume or surface a positive and in another part an equal negative charge. In this case, for which a pair of equal and opposite electrons would be the most simple example, the surrounding field is due to (4) and (5). We shall say that a particle of this kind is *electrically polarized* and, denoting by \mathbf{r} the vector drawn from the origin towards the element of volume $d\tau$, we shall call the vector

$$\int \varrho \mathbf{r} d\tau = \mathbf{p} \quad (7)$$

the *electric moment* of the particle. In virtue of the supposition

$$\int \varrho d\tau = 0,$$

this vector is independent of the position of the origin of coordinates. From (7) we may infer immediately

$$\int \varrho x d\tau = p_x, \text{ etc.}, \quad \int \varrho v_x d\tau = \dot{p}_x, \text{ etc.}$$

In all dielectrics, and perhaps in conductors as well, we must admit the existence of particles that may be electrically polarized. We shall refer to their charges by the name of *polarization-electrons*.

c. Finally, let there be a class of particles whose field is solely due to the expressions (6), the integrals (3), (4), (5) being all 0. If we suppose the values of

$$\int \varrho x^2 d\tau, \quad \int \varrho x y d\tau, \quad \int \varrho x z d\tau, \text{ etc.}$$

not to vary in the course of time, we can express all the integrals (6) by means of the vector

$$\frac{1}{2} \int \varrho [\mathbf{v}, \mathbf{v}] d\tau = \mathbf{m}, (8)$$

i. e. of the vector whose components are

$$m_x = \frac{1}{2} \int \varrho (y v_z - z v_y) d\tau, \text{ etc.},$$

Indeed, we shall have

$$\int \varrho v_x x d\tau = 0, \quad \int \varrho v_x y d\tau = -m_z, \quad \int \varrho v_x z d\tau = +m_y, \text{ etc.} \quad (9)$$

The field produced by a particle satisfying the above conditions may be shown to be identical to the field due to a small magnet whose moment is \mathbf{m} . For this reason, we shall speak of a *magnetized particle* and we shall call \mathbf{m} its *magnetic moment*.

According to the view here adopted, this moment is caused by rotating or circulating motions of the charges within the particle, similar to AMPÈRE'S molecular electric currents. If, for the product $e\omega$ of a charge e and its velocity, we introduce the name of "quantity of motion of the charge", the integral in (8) may be said to represent the moment about the origin O of the quantities of motion of all the charges present.

A very simple example is furnished by a spherical shell, rotating round a diameter, and enclosing an immovable, concentric sphere, the shell and the sphere having equal and opposite charges, uniformly distributed.

Whatever be the motion of the charges which call forth the moment m , we may properly apply to them the denomination of *magnetization-electrons*.

§ 5. In the determination of the mean values of the quantities in (I), (II) and (4), the following considerations and theorems will be found of use.

a. Consider a space containing an immense number of points Q , whose mutual distances are of the same order of magnitude as those between the particles of a ponderable body. Let N be the number of these points per unity of volume. If the density of the distribution gradually changes from point to point — in a similar way as may be the case with the observed density of a body — the value of N belonging to a point P is understood to be derived from the number of points Q lying within a physically infinitely small space of which P is the centre.

Draw equal and parallel vectors $QR = r$ from all the points Q , and consider a physically infinitely small plane $d\sigma$ whose normal, drawn towards one of its sides, is n . The question is to find the number of the vectors QR that are intersected by the plane, a number which we shall call positive if the ends of the vectors, and negative if their starting points lie on the side of $d\sigma$ indicated by n .

If N has the same value throughout the whole space, and if the points Q are *irregularly* distributed, like the molecules of a liquid or a gas, the number in question will be the same for all equal and parallel planes, whence it is easily found to be

$$N r_n d\sigma \dots \dots \dots (10)$$

The problem is somewhat less simple if the points Q have a regular geometric arrangement, such as those one considers in the theory of the structure of crystals. If, in this case, the length of the vectors QR is smaller than the mutual distance σ of neigh-

houring points, it may come to pass that there are a certain number of intersections with one plane $d\sigma$ and none at all with another plane of the same direction. We shall meet this difficulty by irregularly undulating the element of surface, in such a way that the distances of its points from a plane $d\sigma$ are of the same order of magnitude as the distance σ , and that the direction of the normal is very near that of the normal n to this plane; so that the extent of the element and the normal to it may still be denoted by $d\sigma$ and n . It is clear that, if N is a constant, the number of intersections of the vectors QR with such an undulated element may again be said to depend only on its direction and magnitude, and that it may still be represented by the formula (10).

The same formula will hold in case the value of N should slowly change from point to point, provided we take for N the value belonging to the centre of gravity of the element.

b. Let us apply the above result to the elements $d\sigma$ of a closed surface σ . Let n_1 be the number of ends R , and n_2 the number of starting points Q lying within σ .

Supposing the normal n to be drawn in the outward direction, we may write for the difference of these numbers

$$n_1 - n_2 = - \int N r_n d\sigma, \quad . \quad . \quad . \quad . \quad . \quad (11)$$

an expression, which of course can only be different from 0, if N changes from point to point.

c. Leaving the system of points, we pass to a set of innumerable equal particles, distributed over the space considered. Let q be a scalar quantity, whose values in the points $A_1, A_2, \dots A_k$ of one of the particles are $q_1, q_2, \dots q_k$, the position of these points and the values of q being the same in all particles, and these values being such that

$$q_1 + q_2 + \dots + q_k = 0 \quad . \quad . \quad . \quad . \quad . \quad (12)$$

We proceed to determine the sum Σq of the values q , belonging to all the points A that lie within the above mentioned closed surface σ . Of course, the particles lying completely within the surface will contribute nothing to this sum. Yet, it may be different from 0, because a certain number of particles are cut in two by the surface, so that only a part of the values $q_1, q_2, \dots q_k$ belonging to each of these are to be taken into account.

Assume in each particle an origin O (having the same position in each) and regard this as composed of k points $O_1, O_2, \dots O_k$. Attach to these the values $-q_1, -q_2, \dots -q_k$. Then, in virtue

of (12), we may, without changing the sum Σq , include in it not only the points A , but likewise the points O . Now, if the vectors $O_1 A_1, O_2 A_2, \dots, O_k A_k$ are denoted by r_1, r_2, \dots, r_k , the part of Σq due to the points O_1 and A_1 will be

$$-\int N q_1 r_{1n} d\sigma,$$

as may easily be inferred from (11). There are similar expressions for the parts of the sum corresponding to O_2 and A_2, O_3 and A_3 , etc. Hence, if we introduce for a single particle the vector

$$q = \Sigma q r. \quad (13)$$

and if we put

$$N q = \Omega, \quad (14)$$

the final result will be

$$-\int \Omega_n d\sigma \quad (15)$$

In this formula, the vector Ω is to be considered as a function of the coordinates because the number N may gradually change from one point to another (this \S, a) and the vector q may vary in a similar way. If now the surface σ is taken physically infinitely small, though of so large dimensions that it may be divided into elements, each of which is large in comparison with molecular dimensions, the expression (15) may, by a known theorem, be replaced by

$$- \text{Div } \Omega. S, \quad (16)$$

S being the space within the surface σ .

d. It has been assumed till now that the quantity q occurs only in a limited number of points within each particle. By indefinitely increasing this number k , we obtain the case of a quantity q continuously distributed. We shall then write $q d\tau$ instead of q , and replace the sums by integrals. The condition (12) becomes

$$\int q d\tau = 0,$$

which we shall suppose to be fulfilled for each separate particle, the vector q is now to be defined by the equation

$$q = \int q r d\tau, \quad (17)$$

and the sum Σq , whose value we have calculated, becomes $\int q d\tau$, taken for the space enclosed by σ . If we still understand by Ω the vector given by (14), the value of the integral for a physically infinitely small space will be

— $\text{Div } \mathfrak{Q}$. S.

Now, according to the definition of mean values (§ 3), division of this by S will give the mean of q ; hence

$$q = -\text{Div } \mathfrak{Q}. \quad (18)$$

This result may even be extended to a state of the body, in which the distribution of the values of q is not the same in neighbouring particles. In this case we may again apply to each particle the formula (17), but \mathfrak{Q} can no longer be calculated by (14). We have now to define this vector by

$$\mathfrak{Q} = \frac{1}{S} \sum \mathfrak{q}, \quad (19)$$

the sum being taken for all the particles that lie wholly in the space S, without attending to those that are cut in two by the surface. We may express this in words by saying that \mathfrak{Q} is the sum of all the vectors \mathfrak{q} , reckoned per unit of volume.

e. The case still remains that a quantity q , given for every point, has such values that the integral $(q) = \int q d\mathbf{r}$, taken for a single particle, is not 0. If this quantity were constant throughout the space occupied by a particle, it would be unnecessary to take into account those which are cut in two by the surface σ and we should have

$$\bar{q} = N(q).$$

The most general case may be reduced in the following way to this case and to those that have already been disposed of before. If q is distributed in some arbitrary manner, we begin by calculating for a single particle the mean value $q_1 = \frac{1}{s}(q)$, s being the volume of the particle, and we put in every point $q = q_1 = q_2$. We shall then have

$$\bar{q} = \bar{q}_1 + \bar{q}_2.$$

The problem is therefore reduced to the determination of two mean values, one of which may be found by what has just been said, and the other by applying the formula (18).

§ 6. The mean value of each of the quantities \mathfrak{q} and $\mathfrak{q} \mathfrak{v}$ in the equations (I), (II) and (I) may be decomposed into three parts, belonging to the conduction-electrons, the polarization-electrons and the magnetization-electrons. In determining them, we shall suppose the ponderable matter to have a visible motion with velocity \mathfrak{w} , and we shall write \mathfrak{v} for the velocity the charged matter may have in addition to this. We have therefore to replace \mathfrak{v} by $\mathfrak{w} + \mathfrak{v}$, and to determine separately $\bar{\mathfrak{q} \mathfrak{w}}$ and $\bar{\mathfrak{q} \mathfrak{v}}$.

a. Conduction-electrons. The mean value of \mathfrak{q} , in so far as it depends on these, may be called the (*measurable*) *density of electric charge*; we shall denote it by \mathfrak{q}_1 .

The mean value \mathfrak{E} of $\mathfrak{q} \mathfrak{w}$ may be represented by

$$\mathfrak{E} = \mathfrak{q}_1 \mathfrak{w}.$$

This is the *convection-current*, and the vector

$$\mathfrak{J} = \mathfrak{q} \mathfrak{v},$$

taken for the conduction-electrons, may fitly be called the *conduction-current*.

b. Polarization-electrons. Let the body contain innumerable particles electrically polarized, each having an electric moment \mathfrak{p} . The vector defined by the equation

$$\mathfrak{P} = \frac{1}{8} \Sigma \mathfrak{p}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

where the sign Σ is to be understood in the same sense as in the formula (19), is the *electric moment for unit volume* or the *electric polarization* of the body. Replacing q by \mathfrak{q} in the formulae of § 5, *d*, and taking into account (7), we find for the part of \mathfrak{q} that is due to the polarization-electrons,

$$\mathfrak{Q}_2 = - \text{Div } \mathfrak{P}.$$

We may next remark that the visible velocity \mathfrak{w} is practically the same in all points of a particle. Since, for the space occupied by it,

$$\int \mathfrak{q} \, d\tau = 0,$$

we have likewise

$$\int \mathfrak{q} \, \mathfrak{w}_x \, d\tau = \int \mathfrak{q} \, \mathfrak{w}_y \, d\tau = \int \mathfrak{q} \, \mathfrak{w}_z \, d\tau = 0,$$

so that the values of $\mathfrak{q} \, \overline{\mathfrak{w}_x}$, $\mathfrak{q} \, \overline{\mathfrak{w}_y}$, $\mathfrak{q} \, \overline{\mathfrak{w}_z}$ may be found by means of (18). The result is

$$\overline{\mathfrak{q} \, \mathfrak{w}_x} = - \text{Div } (\mathfrak{w}_x \mathfrak{P}), \quad \text{etc.} \quad . \quad . \quad . \quad . \quad . \quad (21)$$

We have finally to determine $\overline{\mathfrak{q} \, \mathfrak{v}}$. Now, the quantities $\mathfrak{q} \mathfrak{v}_x$, $\mathfrak{q} \mathfrak{v}_y$, $\mathfrak{q} \mathfrak{v}_z$ are of the kind considered at the end of § 5, *e*. However, there are cases, especially if the velocities \mathfrak{v}_x , \mathfrak{v}_y , \mathfrak{v}_z and the dimensions of the particles are sufficiently small, in which the parts of $\overline{\mathfrak{q} \mathfrak{v}_x}$, $\overline{\mathfrak{q} \mathfrak{v}_y}$, $\overline{\mathfrak{q} \mathfrak{v}_z}$ corresponding to $\overline{q_2}$ of § 5, *e*, may be neglected. Confining ourselves to such cases, we shall determine $\overline{\mathfrak{q} \mathfrak{v}}$ without taking into consideration the particles intersected by the surface σ .

For a single particle we may write

$$\int \mathfrak{Q} \mathfrak{v} d\tau = \frac{d\mathfrak{p}}{dt},$$

and for a physically infinitely small space, partaking of the visible motion

$$\int \mathfrak{Q} \mathfrak{v} d\tau = \frac{d}{dt} \Sigma \mathfrak{p}.$$

On account of (20) this is equal to

$$\frac{d}{dt} (S \mathfrak{P}),$$

so that

$$\overline{\mathfrak{Q} \mathfrak{v}} = \frac{1}{S} \int \mathfrak{Q} \mathfrak{v} d\tau = \frac{1}{S} \frac{d}{dt} (S \mathfrak{P}).$$

In performing the differentiation we must attend to the change of \mathfrak{P} in a point that moves with the velocity \mathfrak{w} . If $\dot{\mathfrak{P}}$ relates to a fixed point of space, we have

$$\frac{d\mathfrak{P}}{dt} = \dot{\mathfrak{P}} + \mathfrak{w}_x \frac{\partial \mathfrak{P}}{\partial x} + \mathfrak{w}_y \frac{\partial \mathfrak{P}}{\partial y} + \mathfrak{w}_z \frac{\partial \mathfrak{P}}{\partial z},$$

and, since

$$\frac{dS}{dt} = S \cdot \text{Div } \mathfrak{w},$$

$$\overline{\mathfrak{Q} \mathfrak{v}} = \dot{\mathfrak{P}} + \mathfrak{w}_x \frac{\partial \mathfrak{P}}{\partial x} + \mathfrak{w}_y \frac{\partial \mathfrak{P}}{\partial y} + \mathfrak{w}_z \frac{\partial \mathfrak{P}}{\partial z} + \mathfrak{P} \text{Div } \mathfrak{w}.$$

Combining this with (21), we get for the mean value of the current corresponding to the motion of the polarization-electrons

$$\dot{\mathfrak{P}} + \text{Rot} [\mathfrak{P} \cdot \mathfrak{w}].$$

c. Magnetization-electrons. If the body contains magnetized particles (§ 4, *c*), we have nothing to add to \mathfrak{Q} and $\overline{\mathfrak{Q} \mathfrak{v}}$. There will however be a new part of $\mathfrak{Q} \mathfrak{v}$. We can calculate it by applying (18), because the quantities (5) vanish for every particle.

Let us first replace, in the formulae of § 5 *d*, q by $\mathfrak{Q} \mathfrak{v}_x$. We then find

$$\mathfrak{Q}_x = 0, \quad \mathfrak{Q}_y = -\mathfrak{m}_z, \quad \mathfrak{Q}_z = +\mathfrak{m}_y,$$

and, if we denote by \mathfrak{M} the *magnetic moment for unit volume* or the *magnetization*, a vector that is to be defined in a similar way as \mathfrak{P} ,

$$\mathfrak{Q}_x = 0, \quad \mathfrak{Q}_y = -\mathfrak{M}_z, \quad \mathfrak{Q}_z = +\mathfrak{M}_y.$$

Finally, by (18),

$$\overline{\mathfrak{Q} \mathfrak{v}_x} = \frac{\partial \mathfrak{M}_z}{\partial y} - \frac{\partial \mathfrak{M}_y}{\partial z},$$

with similar expressions for $\mathfrak{Q} \mathfrak{v}_y$ and $\mathfrak{Q} \mathfrak{v}_z$.

We may further deduce from (1), taking into account (I) and (II),

$$\operatorname{Div} \mathfrak{g} = 0,$$

and consequently

$$Div \bar{\mathfrak{g}} = 0.$$

Now the expression $Rot \mathfrak{M}$ we have found for the current that is equivalent to the magnetization, shows immediately that the distribution of this current, taken by itself, is solenoidal. We conclude from this that

[illegible]

From (III) we may deduce, if we introduce the value (26),

$$Rot \mathfrak{B} = 4 \pi \mathfrak{S} + 4 \pi Rot \mathfrak{M},$$

or, taking into account the relation

$$\mathfrak{V} = \mathfrak{H} + 4\pi \mathfrak{M}$$

which results from (27) and (28),

$$Rot \mathfrak{H} = 4 \pi \mathfrak{E} . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (III')$$

Finally we find by (IV)

$$Rot \, \mathfrak{G} = - \mathfrak{L} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (IV')$$

and by (V)

$$Div \mathfrak{B} = 0. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (V')$$

We have thus been led back to the equations of the electromagnetic field in a form that has long been known. In this form we may use them without even thinking of the individual electrons. As soon however as we seek to penetrate into the mechanism producing the phenomena, we must keep in mind the definitions that have been given of the different quantities appearing in the equations and the manner in which they are connected with the distribution and the motion of the elementary electric charges. The formulae (27) and (28) e. g. show the precise meaning that is to be attached in the theory of electrons to the terms "magnetic force" and "magnetic induction".

The equations (I')—(V') may be applied to all bodies indifferently. It is otherwise with the formulae expressing the relation between \mathfrak{S} (or \mathfrak{D}) and \mathfrak{E} , and that between \mathfrak{B} (or \mathfrak{M}) and \mathfrak{H}' ; the form of these depends entirely on the particular properties of the bodies considered. I shall not here discuss these more special formulae; in order to deduce them from the theory of electrons it is necessary to consider the forces acting on the electrons in a conductor, the "molecular motion" of these particles and the circumstances which determine the electric and magnetic moments of a single molecule or atom.

¹⁾ See VOIGT, Elektronenhypothese und Theorie des Magnetismus. Nachr. d. Ges. d. Wiss. zu Göttingen, 1901, Heft. 3.

Astronomy. — *"Preliminary investigation of the rate of the standard clock of the observatory at Leyden HOHWÜ N°. 17 after it was mounted in the niche of the great pier."* By Dr. E. F. VAN DE SANDE BAKHUYZEN.

1. In a preceding paper on the clock HOHWÜ 17 I communicated the investigations I had made on an inequality of a yearly period noted in its rate which does not depend on the actual temperature.

Besides the periods 1861—1874 and 1877—1898 I discussed also the period 1899—1902 when the clock had been mounted in the hall of the observatory in a niche cut out for this purpose from the great pier. From the mean daily rates during periods of about a month each, I derived formulae for the rate in two different ways, and this research clearly brought to light that during this period the rate of the clock had become considerably more regular than before and now satisfies high demands.

Since that time the same formulae have been compared with the daily rates observed during much shorter periods and an investigation has been undertaken about the barometer coefficient, for which purpose the monthly rates were less appropriate.

The latter calculations have so clearly shown the excellence of the clock also with regard to its rate during periods of a few days, that it seemed to be of interest briefly to give here the results to which they led.

2. The results we obtained from the previous investigations may be resumed thus.

Under all the conditions in which the clock HOHWÜ 17 has been placed, its rate, after correction for the influence of the temperature, has always shown a residual yearly inequality. As the former influence had been derived from the yearly variation of the temperature, the residual inequality must necessarily show a difference of phase of three months with respect to the temperature.

If the influence of the temperature had been derived and accounted for in the form $c_1(t-t_0) + c_2(t-t_0)^2$, whether we had found for c_2 a small negligible value, as in the period 1862—1874 or an obviously real quantity as in the period 1899—1902, the residual inequality could with sufficient accuracy be expressed by a simple sinusoid. If on the contrary only a linear influence of the temperature had been accounted for, while an investigation of c_2 showed it to have an appreciable value, the residual inequality showed a half-yearly term besides. This could be expected; for as long as only the

yearly variation of the temperature is concerned, a quadratic influence of the latter and a half-yearly inequality are completely equivalent.

3. For the rate of the clock during the period 1899—1902 I derived in the first place the formula:

$$D. R. = -0^{\circ}.169 + 0^{\circ}.0140(h-760). \\ -0^{\circ}.0253(t-10^{\circ}) + 0^{\circ}.00074(t-10^{\circ})^2. \\ + 0^{\circ}.0465 \cos 2\pi \frac{T-May 3}{365} D$$

secondly the formula :

$$D. R. = -0.157 + 0.0140 (h - 760) - 0.0220 (t - 10^0) + \text{Suppl. inequal. II}$$

The supplementary inequality in the second formula was represented by a curve. Yet it can as well be represented by a yearly and a half-yearly term. We then find:

$$\begin{aligned} \text{Suppl. Inequ.} = & + 0^{\text{s}}.0471 \cos 2\pi \frac{T - \text{Apr. 29}}{365} \\ & - 0^{\text{s}}.0198 \cos 4\pi \frac{T - \text{Apr. 16}}{365} . . . \quad II) \end{aligned}$$

From the term depending on the square of the temperature found by the first method of calculation and from the yearly variation of the temperature in the clock-case, which is approximately represented by

$$t = +11^{\circ}.6 + 6^{\circ}.54 \sin 2\pi \frac{T - \text{May } 4}{365} \quad 1)$$

we derive for the half-yearly term

$$- 0^s.0158 \cos 4\pi \frac{T - \text{May } 4}{365}$$

which is in sufficient agreement.

The two formulae must however give different results, as soon as the accidental variations of the temperature become of importance, and therefore it was of interest to compare the rates during short periods with either.

4. Hence two comparisons were made for the three years 1899 May 3—1902 May 3. *)

1) For the next term we find: $+ 0.55 \sin 4\pi \frac{T - \text{June } 9}{365}$.

²⁾ In this and the following calculations the supplementary inequality for formula II was read from the curve.

Within that period I could dispose of 182 time-determinations at average intervals of 6 days, giving 181 values for the daily rate. We can assume as mean error of the result of a time-determination, largely accounting for systematic errors such as variations of the personal errors of the observers, ± 0.04 .

I do not give here in full the results of the comparison of these 181 observed rates with the two formulæ and only lay down the mean values found in both cases for a difference: observation—computation.

I found:

Formula I M. Diff. = ± 0.0333

 " II ± 0.0344

Hence this mean difference is nearly the same for the two formulæ; indeed, if the three years are kept apart, it is found to be a little greater for formula I in two of the three years.

We may therefore say that the two are in equally good agreement with the observations and for the investigation of the barometer coefficient it was sufficient to use either.

I chose formula II (linear influence of the temperature) and I proceeded in the following way. The rates reduced with that formula to 760 m.m. and 10° and freed from the supplementary inequality were divided into five groups according to the barometric pressure and for each group the mean of those reduced rates was calculated. The results are laid down in the following table, where the first column gives the number of rates from which each mean has been derived.

Number.	Barom.	Reduced. D. R.	O.—C.
17	752.8	— 0 ^s .174	— 0 ^s .002
31	757.6	162	+ 02
68	762.6	154	+ 01
44	767.4	145	+ 02
21	772.2	141	— 02

From these results I derived as correction for the barometer coefficient:

$$\Delta b = + 0.0017$$

while I found for the daily rate for 760 mm. — 0^s.160. With these values we obtain a very good agreement with the observations as appears from the differences obs.—comp. contained in the last column of the foregoing table. Hence it appears that the value for the barometer coefficient $b = + 0^s.0157$ is determined with great precision ¹⁾.

For the constant term of the formula we find from all the rates — 0^s.161, while, if we put $b = + 0^s.0157$ also in formula I, the constant term here becomes — 0^s.173.

5. With the formulae thus modified:

$$\begin{aligned} D. R. &= - 0^s.173 + 0^s.0157 (h-760). \\ &\quad - 0^s.0253 (t-10^\circ) + 0^s.00074 (t-10^\circ)^2. \\ &\quad + \textit{Supplementary inequality} (Ia). \\ D. R. &= - 0^s.161 + 0^s.0157 (h-760). \\ &\quad - 0^s.0220 (t-10^\circ) + \textit{Supplem. inequal.} . . , (IIa). \end{aligned}$$

we have again compared all the observed rates and this time the comparison has been extended to 1902 Sept. 20 i. e. till almost five months after the period from which the formulae were derived. Besides the observations have been compared with a third calculation. This we obtained by applying the formula IIa so that we did not use the actual mean temperature but that of five days earlier. It is obvious that in doing so also the value of the supplementary inequality must be altered. An assumed lagging behind of the influence of the temperature of five days is equal, so far as the general variation of the temperature (as found above) is concerned, to $0.27 \times$ the yearly supplementary term. Hence the latter had to be diminished by this part of its amount. The formula thus modified I call IIb.

The results of these three comparisons are given in full in the following table. The first column gives the dates of the time determinations, the next column gives the mean temperature for the period between the date of one line above and of that on the same line, while the third, fourth and fifth columns give the differences between the observed rates for those periods and the computations Ia, IIa and IIb respectively. These differences are expressed in thousandth parts of seconds.

¹⁾ According to the investigations of Mr. WEEDE a value little different from this follows for the period 1882—1898.

	Temp.	Obs. — Ia	Obs. — IIa	Obs. — IIb		Temp.	Obs. — Ia	Obs. — IIa	Obs. — IIb
1899					1899				
May 3					Nov. 12	+12.6	— 12	— 14	— 28
» 12	+10.5	— 11	— 18	— 10	» 20	11.0	— 3	— 8	+ 3
» 17	12.0	+ 33	+ 23	+ 9	» 28	10.8	— 42	— 51	— 63
» 30	12.7	0	— 12	— 1	Dec. 7	10.4	— 9	— 22	— 19
June 3	13.0	— 17	— 32	— 40	» 13	6.8	+ 83	+ 83	+140
» 8	14.8	+ 43	+ 33	— 3	» 16	3.7	+ 76	+103	+170
» 14	14.8	+ 27	+ 14	+ 23	» 19	3.0	— 19	+ 16	+ 52
» 22	15.4	+ 36	+ 22	+ 12	» 23	2.3	— 24	+ 21	+ 31
» 27	16.5	+ 20	+ 11	+ 5	» 31	3.1	— 52	— 19	— 38
July 7	16.5	+ 7	— 3	+ 7	1900				
» 11	16.4	— 17	— 29	— 28	Jan. 8	5.3	— 32	— 26	— 62
» 14	18.1	+ 57	+ 57	+ 13	» 20	5.4	— 44	— 39	— 36
» 17	18.6	+ 56	+ 60	+ 29	» 25	6.0	— 36	— 36	— 62
» 25	19.6	+ 78	+ 91	+ 71	Febr. 4	6.1	— 12	— 9	— 2
» 31	19.6	+ 39	+ 50	+ 60	» 8	4.9	— 22	— 6	+ 8
Aug. 3	19.4	+ 30	+ 38	+ 45	» 20	4.3	— 28	— 2	+ 3
» 9	19.6	+ 66	+ 76	+ 71	March 2	6.9	— 4	0	— 28
» 14	19.1	+ 21	+ 28	+ 44	» 9	6.3	— 18	— 7	+ 23
» 21	18.7	+ 26	+ 30	+ 34	» 16	6.7	— 40	— 30	— 34
» 26	17.7	— 3	— 4	+ 12	» 20	6.8	— 30	— 20	— 10
Sept. 3	18.3	+ 17	+ 25	+ 11	» 26	6.6	— 25	— 12	— 1
» 8	18.3	+ 9	+ 22	+ 18	» 30	6.1	— 45	— 26	— 7
» 13	17.7	+ 34	+ 44	+ 50	April 2	6.0	— 52	— 32	— 18
» 21	16.3	— 14	— 9	+ 7	» 4	6.1	— 38	— 19	— 11
Oct. 5	14.4	— 35	— 32	— 24	» 12	7.2	— 12	— 1	— 11
» 9	13.1	+ 3	+ 7	+ 15	» 18	9.0	— 29	— 29	— 49
» 16	11.9	— 9	— 5	+ 8	» 21	9.9	+ 37	+ 34	+ 25
» 19	11.1	— 42	— 37	— 30	» 24	10.7	+ 17	+ 9	— 11
» 24	10.9	— 19	— 14	— 17	» 28	10.1	— 16	— 20	— 1
» 31	11.4	— 15	— 12	— 35	May 1	9.8	+ 14	+ 10	+ 35
Nov. 5	12.3	+ 4	+ 6	— 21	» 4	10.4	— 71	— 77	— 83

	Temp.	Obs. — Ia	Obs. — IIa	Obs. — IIb		Temp.	Obs. — Ia	Obs. — IIa	Obs. — IIb
1900					1900				
May 10	+12.1	— 12	— 22	— 43	Oct. 19	+12.6	— 7	— 3	+ 34
» 14	11.7	— 16	— 26	— 3	» 29	11.6	— 9	— 6	— 3
» 23	11.2	— 19	— 30	— 12	Nov. 3	11.8	— 50	— 48	— 67
» 26	12.5	— 11	— 22	— 46	» 7	11.3	— 13	— 13	— 14
June 2	13.0	— 27	— 40	— 43	» 16	10.3	— 1	— 2	+ 6
» 9	14.9	— 9	— 19	— 44	» 23	9.2	+ 22	+ 20	+ 22
» 12	16.3	— 26	— 31	— 48	» 27	8.8	— 12	— 14	— 20
» 18	17.3	+ 33	+ 33	+ 15	Dec. 7	8.3	+ 21	+ 17	+ 14
» 23	17.1	— 29	— 33	— 21	» 10	8.9	— 62	— 75	— 106
» 28	16.6	— 11	— 20	+ 2	» 15	9.3	+ 23	+ 6	— 14
July 2	16.2	— 46	— 58	— 45	» 19	9.5	+ 50	+ 29	+ 14
» 10	16.3	— 31	— 43	— 36	» 29	8.7	+ 55	+ 34	+ 42
» 13	16.4	— 29	— 40	— 40	1901				
» 17	18.1	+ 18	+ 18	— 24	Jan. 3	7.4	+ 69	+ 57	+ 64
» 21	19.8	+ 31	+ 46	— 4	» 6	5.2	+ 96	+ 103	+ 162
» 25	20.8	+ 41	+ 68	+ 39	» 11	3.1	+ 59	+ 91	+ 146
» 31	20.7	+ 11	+ 35	+ 36	» 14	3.0	— 32	+ 2	0
Aug. 7	19.0	— 39	— 35	— 4	» 17	3.2	+ 27	+ 57	+ 50
» 11	17.5	— 43	— 51	— 21	» 23	4.7	+ 37	+ 51	+ 18
» 14	17.1	— 63	— 74	— 61	Febr. 1	6.8	+ 47	+ 43	+ 18
» 17	17.6	— 46	— 51	— 60	» 4	6.0	+ 26	+ 31	+ 49
» 23	18.8	+ 4	+ 12	— 25	» 11	5.1	+ 32	+ 46	+ 67
» 28	18.4	— 28	— 22	— 11	» 20	4.4	+ 15	+ 39	+ 55
» 31	17.4	— 34	— 34	— 8	March 5	5.4	+ 28	+ 44	+ 27
Sept. 4	16.9	— 25	— 27	— 20	» 13	7.2	+ 4	+ 9	+ 14
» 12	16.4	— 48	— 48	— 44	» 21	7.2	— 10	— 3	+ 1
» 16	16.2	— 32	— 29	— 35	» 25	6.3	+ 1	+ 17	+ 50
» 19	16.5	+ 3	+ 11	— 1	Apr. 1	5.8	— 28	— 6	+ 13
» 29	16.4	— 31	— 20	— 27	» 4	7.3	— 5	+ 6	— 24
Oct. 6	15.3	— 24	— 14	— 6	» 7	8.2	+ 12	+ 16	— 14
» 16	14.6	— 12	— 3	— 3	» 17	9.3	+ 3	+ 9	2

	Temp.	Obs. — Ia	Obs. — IIa	Obs. — IIIb		Temp.	Obs. — Ia	Obs. — IIa	Obs. — IIIb
1901					1901				
Apr. 20	+ 9.3	+ 21	+ 20	+ 35	Nov. 4	+44.9	+ 6	+ 8	+ 44
» 23	40.5	+ 38	+ 32	+ 42	» 4	40.6	+ 26	+ 29	+ 48
» 29	41.6	+ 49	+ 41	+ 24	» 15	9.9	+ 15	+ 19	+ 44
May 3	41.7	+ 13	+ 4	+ 18	» 22	9.6	+ 37	+ 35	+ 37
» 8	41.6	— 5	— 15	— 3	» 26	9.0	+ 53	+ 50	+ 51
» 11	41.5	+ 4	— 8	+ 8	Dec. 6	8.4	— 3	— 7	— 40
» 14	41.7	— 4	— 11	— 3	» 16	7.8	+ 9	+ 4	+ 7
» 20	41.9	— 8	— 19	— 12	» 25	5.5	+ 4	+ 7	+ 25
June 2	44.0	+ 15	+ 5	— 15	1902				
» 7	46.4	+ 17	+ 14	0	Jan. 5	6.6	— 6	— 11	— 43
» 18	45.6	— 30	— 39	— 10	» 11	8.6	+ 20	0	— 19
» 25	45.3	— 28	— 42	— 43	» 18	8.1	— 24	— 40	— 30
July 3	46.8	— 16	— 24	— 38	» 28	7.9	+ 18	+ 5	+ 5
» 10	47.7	— 19	— 22	— 30	Febr. 1	6.4	+ 36	+ 37	+ 70
» 15	49.1	— 6	+ 3	— 24	» 7	4.9	— 3	+ 13	+ 45
» 20	49.8	— 2	+ 14	+ 2	» 12	4.6	— 44	— 24	— 15
» 31	20.2	+ 4	+ 21	+ 23	» 15	4.2	— 36	— 11	0
Aug. 9	49.5	— 28	— 18	— 11	» 20	3.2	— 68	— 29	— 2
» 12	49.6	+ 14	+ 25	+ 16	» 24	4.0	— 7	+ 23	+ 12
» 16	49.4	— 4	+ 7	+ 3	March 4	5.6	— 14	+ 4	— 25
» 22	48.9	— 37	— 30	— 22	» 10	7.0	— 15	— 9	— 23
» 27	48.5	— 25	— 18	— 13	» 14	7.1	+ 9	+ 16	+ 25
Sept. 5	46.8	— 24	— 27	— 7	» 19	7.7	+ 12	+ 15	+ 12
» 16	45.8	— 22	— 23	— 26	Apr. 3	8.3	+ 12	+ 14	+ 21
» 20	45.5	+ 9	+ 11	+ 16	» 8	8.2	— 3	+ 4	+ 11
» 26	46.2	+ 20	+ 29	+ 7	» 12	8.0	— 14	— 7	+ 8
Oct. 4	46.7	— 5	+ 9	— 8	» 18	9.3	+ 32	+ 31	+ 16
» 11	45.5	+ 6	+ 18	+ 30	» 25	11.3	+ 41	+ 34	+ 10
» 16	43.1	+ 7	+ 12	+ 32	» 28	12.1	+ 37	+ 29	+ 26
» 22	42.9	+ 2	+ 6	— 4	May 3	11.0	— 6	— 14	+ 22
» 26	42.6	— 16	— 13	— 16	» 9	10.7	+ 2	— 7	+ 12

	Temp.	Obs. — Ia	Obs. — IIa	Obs. — IIb		Temp.	Obs. — Ia	Obs. — IIa	Obs. — IIb
1902					1902				
May 24	+10.4	— 10	— 18	— 9	July 31	+17.1	— 52	— 63	— 55
» 31	12.7	+ 26	+ 12	— 13	Aug. 5	16.8	— 54	— 68	— 61
June 11	15.9	+ 37	+ 32	+ 16	» 11	16.9	— 40	— 53	— 56
» 17	14.6	— 34	— 48	— 19	» 15	16.0	— 52	— 70	— 50
» 23	15.1	— 13	— 29	— 34	» 20	16.5	— 14	— 28	— 38
» 28	16.8	+ 7	0	— 28	» 25	16.8	— 49	— 55	— 66
July 5	18.4	+ 14	+ 18	0	Sept. 3	17.1	— 16	— 19	— 36
» 12	17.9	— 20	— 21	— 7	» 8	17.8	— 25	— 18	— 31
» 15	17.4	— 31	— 38	— 21	» 14	16.7	— 19	— 16	— 3
» 23	17.7	— 26	— 32	— 47	» 20	15.2	— 27	— 28	— 7

From these differences we derive the following mean errors of a rate computed by means of the three formulae:

	Form. Ia.	Form. IIa.	Form. IIb.
1899 May—1900 April.....	$\pm 0^s.0343$	$\pm 0^s.0345$	$\pm 0^s.0424$
1900 May—1901 April....	345	387	447
1901 May—1902 Sept.....	251	266	274
1899 May—1902 April.....	± 0.0314	± 0.0327	± 0.0385
1899 May—1902 Sept.....	± 0.0341	± 0.0332	± 0.0382

First let us compare the mean errors of the three formulae inter se and with the corresponding values formerly obtained for the formulae I and II with the uncorrected barometer coefficient.

Then it appears in the first place from the values for the period 1899 May—1902 April that the correction of the barometer coefficient has markedly improved the agreement with the observations.¹⁾ Secondly it would appear that the quadratic formula now represents the observations a little better than the linear formula, and thirdly we find that the supposition of a lagging behind of the influence of the temperature markedly impairs the agreement.

¹⁾ Each of the three years separately also leads to the same result.

A consideration of the differences obs.—IIa and obs.—IIb shows however, that the latter conclusion does not equally hold good for all parts of the year and that the agreement with formula IIb is especially bad in the winter months. In order to investigate this more closely, I divided the observations into groups of two months and calculated for each group the mean value of the differences, first for each year separately, then after combining the corresponding groups of the different years. The latter values follow here.

	Form. IIa.	Form. IIb.
January, February.....	$\pm 0^s.0402$	$\pm 0^s.0549$
March, April.....*	208	214
May, June.....	285	284
July, August.....	423	368
September, October.....	215	232
November, December.....	369	559

They lead to the singular result that during the four winter months formula II *b* agrees much less with the observations than IIa, whereas in the middle of the summer the agreement with IIb seems to be better, and in the other months both formulae may be said to agree equally well. In this respect the different years practically lead to the same conclusion and hence we cannot say that this has been brought on by entirely accidental causes. However this may be, we are not entitled yet to assume a lagging behind of the influence of the temperature.

Let us now consider separately the results for formula I *a*, which seems to represent the observations with the greatest precision (those for IIa do not essentially differ from them). It will be seen immediately that during the last seventeen months the rate has been considerably more regular than during the first two years¹⁾; a smaller M.E. has been reached although the 5 last of these 17 months were not included for the derivation of the formula. Thus the feature observed before, i.e. the gradual improvement of the regularity of the rate after the mounting of the clock, shows itself once more. The mean result for the whole period (M. E. = $\pm 0^s.0311$) may already be regarded as very satisfactory, and the great regularity represented by a mean difference of $\pm 0^s.0251$ between a daily rate from a 6 days interval and a relatively simple formula gives us a high sense of the supe-

¹⁾ Already at the beginning we had left out the first 4 months after the remounting.

priority of Hohwü 17 in its present state. That this regularity markedly surpasses the one reached formerly is shown also by the results of an investigation of the years 1886—87, which are among those of the greatest regularity in the period 1877—1898. This investigation was made in a similar manner as the present one, the mean interval between the time determinations used was 5 days and the mean error found was $\pm 0^s.0365$.

6. We may also investigate the rates of a clock in such a manner that only the irregularities of a very short period are considered. A simple process for attaining this is to calculate the mean value of the difference between two consecutive reduced daily rates.

Applying this method to Hohwü 17 during the period under consideration ¹⁾ I found:

Mean difference 1899 May—1902 Sept. $\pm 0^s.0313$.

" " 1901 May—1902 Sept. $\pm 0^s.0253$.

From these mean values considered in connection with the mean errors of the rates in 6-daily and in monthly intervals formerly found we can draw some, albeit rough, conclusions about the amount of the perturbations of longer and shorter periods.

The values found, as well those for the whole period as those derived for the last year only, are given in the following table. The columns *A* contain the values found directly, the columns *B* those diminished by the amount that can be ascribed to the errors of observation, assuming $\pm 0^s.04$ as the total mean error of a time-determination. M. E. β of a 6-daily rate stands for the total mean difference from the formula *Ia*, found above, M. E. α represents the error derived from the mean differences between two consecutive rates. The mean errors of the monthly rates differ a little from those of my previous paper as they now also refer to formula *Ia*.

	1899—1902.		1901—1902.	
	A.	B.	A.	B.
M. Diff. of two 6 d. r.	$\pm 0^s.0313$	$\pm 0^s.0267$	$\pm 0^s.0253$	$\pm 0^s.0193$
M. E. α of 6 d. r.		189		137
M. E. β of 6 d. r.	311	297	251	233
M. E. of monthl. r.	209	208	164	163

¹⁾ The rates were reduced by means of formula *IIa*, but a reduction according to *Ia* would practically have led to the same result.

Although these calculations are inaccurate owing also to the fact that the intervals between the time determinations often differ rather much from 6 days, yet it is evident that the M. E. β are much larger than the M. E. α and hence that considerable perturbations of long period exist, as, indeed, a glance at the table of the obs.—comp. also shows. It would be possible to account tolerably well for the values found for the three different mean errors by assuming, quite arbitrarily of course, that there are two kinds of perturbations, one constant during 6 days and another constant during a month. We should then have to assign for the whole period an average value to both of $\pm 0^s.02$ and for 1901—1902 alone one of $\pm 0^s.015$.

There are not many clocks about which investigations have been published, which allow us directly to compare the regularity of their rates with that of HOHWÜ 17 and most of these embrace but a short period.

An investigation extended over 4 years about the standard-clock of the observatory at Leipzig DENCKER 12 has been published by Dr. R. SCHUMANN ¹⁾. He uses 224 time determinations at mean intervals of $6\frac{1}{2}$ days and derives for the rate a formula containing a linear influence of the temperature and of the barometric pressure and besides a term varying with the time elapsed since a zero-epoch. As mean value of the difference obs.—comp. he finds $\pm 0^s.059$ and there is no evidence of a residual yearly inequality. I calculated also the mean value of a difference between two consecutive rates and found $\pm 0^s.055$.

In the latter respect we possess also data about the four normal clocks of the Geodetic Institute at Potsdam. An investigation by Mr. WANACH ²⁾, about the rates during last year gave the following mean differences between consecutive rates after correction for the barometric pressure, while the temperature was kept very nearly constant:

STRASSER 95	$\pm 0^s.054$
RIEFLER 20	± 0.062
DENCKER 27	± 0.047
DENCKER 28	± 0.049 .

These values are considerably larger than that for HOHWÜ 17, but respecting the Potsdam clocks we must keep in view that DENCKER

¹⁾ R. SCHUMANN. Ueber den Gang der Pendeluhr F. DENCKER XII. (Ber. Sächs. Gesellsch. d. Wiss. 1888).

²⁾ Jahresbericht des Direktors des Königlichen Geodätischen Instituts für die Zeit von April 1901 bis April 1902, pg. 35.

27 and 28 had lately been cleaned, while STRASSER 95 during the period of observation had twice been replaced and meanwhile had been exposed to great differences of temperature. For DENCKER 12 at Leipzig also some perturbations from outside shortly before and during the period under consideration are noted.

7. For a clock which is used for astronomical fundamental determinations the regularity of the rate during the 24 hours of the day is of the very highest importance, but it is obvious that only long continued observations reduced with the greatest possible care can give us any information on this subject.

As yet I can only state that we may confidently expect HÖHW 17 not to be inferior in this respect to other clocks kept at constant temperature, seeing that, while the amplitude of the yearly variation of temperature has diminished comparatively little in its present place, the daily variation has almost entirely disappeared.

This will be seen from the following values of the difference between the temperature at 4 o'clock in the afternoon and the mean of the temperatures of the preceding and the following 8 hours in the morning. These differences taken for about 240 days have been combined in 6 two-monthly groups, and their means follow here :

	Temp. 4h—Temp. 20h
January, February.....	+ 0 ^o .09
March, April.....	+ 0.13
May, June.....	+ 0.12
July, August ..	+ 0.20
September, October.....	+ 0.14
November, December.....	+ 0.08

The mean difference is greatest in summer, but even then very small, while no difference ever reaches to 0^o.5.

(October 22, 1902).

KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN
TE AMSTERDAM.

PROCEEDINGS OF THE MEETING
of Saturday October 25, 1902.

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J. E. VERSCHAFFELT: "Contributions to the knowledge of VAN DER WAALS' ψ -surface. VII. The equation of state and the ψ -surface in the immediate neighbourhood of the critical state for binary mixtures with a small proportion of one of the components", p. 321, (with one plate). Continuation p. 336.

J. BOEKE: "On the structure of the light-perceiving cells in the spinal cord, on the neuro-fibrillae in the ganglioncells and on the innervation of the striped muscles in *Amphioxus lanceolatus*". (Communicated by Prof. T. PLACE), p. 350, (with one plate).

The following papers were read:

Chemistry. — *"A representation in space of the regions in which the solid phases, which occur, are the components, when not forming compounds."* By Prof. H. W. BAKHUIS ROOZEBOOM.

(Communicated in the meeting of September 27, 1902).

In the course of my researches, I have often made use of special kinds of graphical representations to indicate the limits of the existence of single phases or complexes of phases. It was only after the year 1896, when it could be taken for granted that the general

character of the equilibria between liquid and vapour in binary systems had become fully understood, that efforts could be made to construct a complete graphical representation of the conditions of equilibrium in which solid phases occur.

The simplest possible case is found when only the two components of the binary system occur as solid phases. For such a case, I have since 1896 arrived at the representation in space of which photographs are given in the accompanying figures. For the case that chemical compounds or mixed crystals occur as solid phases other figures have been constructed which, however, may be deduced in a simple manner from the present ones.

In this figure the length represents the temperature, the breadth the concentrations x of the mixtures which can exist as vapour or liquid, the component A being placed at the left and the component B at the right. The height represents the pressure. The figure does not represent any particular case, but is so constructed that the different details come out plainly and the dimensions are not too great.

We start from the equilibria between liquid and vapour, which researches on the critical constants of mixtures have proved to be capable of representation by a surface of two sheets, the upper part of which represents the liquids and the lower part the vapours. The coexisting conditions of these two must have equal values of p and t and are therefore, situated on a horizontal line which is parallel to the x -axis. The said surfaces meet at the left side in the vapour-pressure line $O_A C$ of the liquid A , at the right side in the vapour-pressure line $O_B D$ of the liquid B and in front in the critical curve CD .

The points in the space between the two surfaces indicate complexes of liquid and vapour. In the representation, this space is massive, like all other spaces which represent complexes of *two* phases.

The surface of two sheets for liquid + vapour is so constructed that A is the substance with the greatest vapour pressure. It has further been assumed that the liquids are miscible in all proportions and that no maxima or minima occur in the equilibrium pressure.

Descending continuously, the surface would reach the absolute zero if A or B or both did not solidify first.

The pure liquids A and B solidify in O_A and O_B ; from there the vapour-pressure lines $O_A I$ and $O_B K$ of the solid substances run in the left and right vertical side-plane.

Considering now the liquid-mixtures with an increasing amount of B , solid A can only be deposited at temperatures lower than O_A . At each temperature there is a definite liquid and a definite vapour

H. W. BAKHUIS ROOZEBOOM. „A representation in space of the regions in which the solid phases, which occur, are the components when not forming compounds.

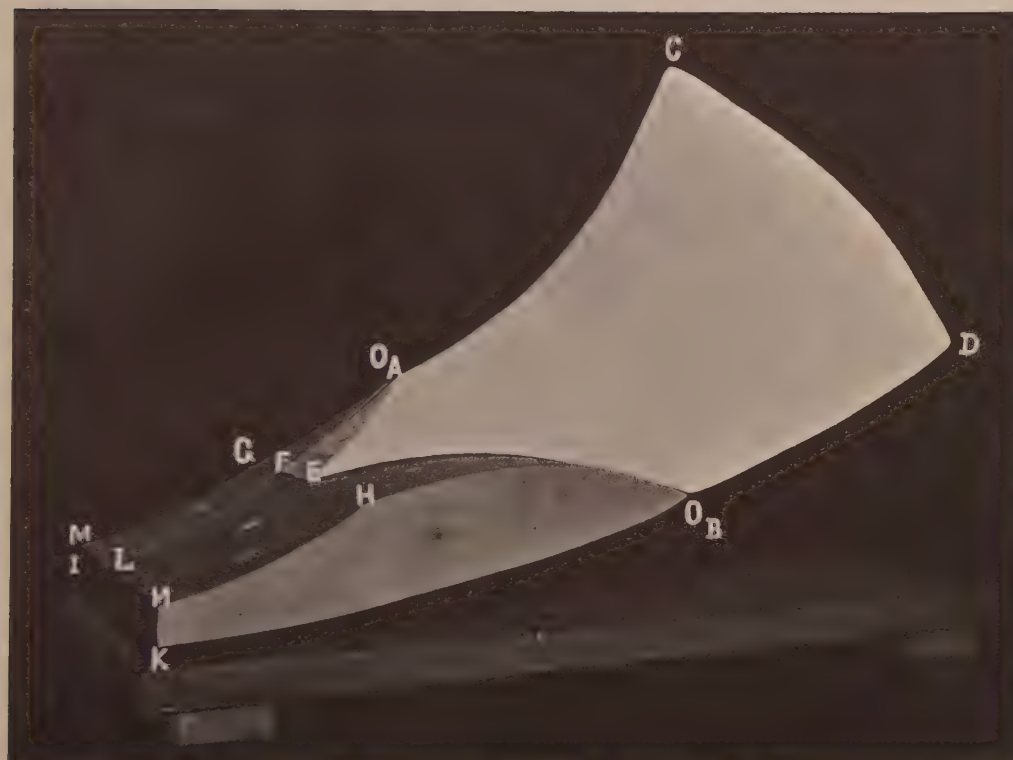


Fig. 1.



Fig. 2.

which coexist with the solid phase A at a definite pressure which is larger than the vapour-pressure of solid A alone, but the same for each of them. The three coexisting phases are represented by the lines $O_A G$, $O_A F$, $O_A E$ respectively standing for solid, gas and liquid. They are situated together on a cylindrical surface, because for equal t , also p is equal. The part $FO_A E$ is also a limitation of the surface of two sheets.

In the same manner we have for the equilibrium of solid B with liquid and vapour the three lines $O_B H$, $O_B E$, $O_B F$, for solid, liquid and gas respectively, again situated on a cylindrical surface, while the part $EO_B F$ thereof forms below a second limitation of the surface of two sheets. This cylindrical surface first rises from O_B but afterwards falls again.

The surface of two sheets terminates, as far as the liquid-surface is concerned, finally in E , the gas-surface in F . This liquid and this vapour may exist in contact with solid A (point G) and also with solid B (point H). As the points G , F , E , H belong to the same values of p and t , they are situated on a horizontal line and represent the only possible complex of four phases.

To the gas-line $O_A F$ a second gas-surface joins, representing the vapours capable of coexisting with solid A , when the quantity of B in the vapour increases; also to $O_B F$ the gas-surface for the vapours in equilibrium with solid B with increasing amounts of A . From the melting points of the pure substances down to the temperature of the quadruple-point $G F E H$ these two gas-surfaces are not in contact with each other, but each of them singly is in contact with the gas-surface of the surface of two sheets.

Below that temperature they intersect each other immediately, forming the line FL which represents the vapours capable of coexisting with solid $A +$ solid B . To this belong the lines GM for solid A and HN for solid B which are again situated on a cylindrical surface.

All complexes of the solid phase A and of the coexisting vapours are situated within the space formed by the gas-surface $IO_A FL$, the surface of the solid phase $IO_A GM$ and the two cylindrical surfaces $GO_A F$ and $MGFL$. All complexes of the solid phase B and the vapours which can exist in contact with it, are situated in the space bounded by the gas-surface $KO_B FL$, the surface of the solid phase $KO_B HN$ and the cylindrical surfaces $HO_B F$ and $NHFL$.

Both spaces extend to the absolute zero if no new phases are formed.

The three surfaces representing the equilibria of gas with liquid, with

solid A and with solid B meet each other in the point F . In the same way, two other liquid-surfaces must join in the point E at which the liquid surface coming from higher temperatures ends, namely those which indicate the p, t, x values of the liquids which can coexist with solid A or solid B . The lower limits of these surfaces are the lines $O_A E$ and $O_B E$ which represent the equilibrium of solid and vapour. Setting out from these lines the vapour disappears when the pressure is increased. On account of the small changes which the composition of the liquid undergoes with an increase of pressure, the liquid-surfaces $O_A EPU$ and $O_B EPV$ will rise almost vertically. They terminate to the left and the right in the melting point lines $O_A V$ and $O_B V$ of the solid substances A and B , whilst they intersect each other in the line EP which indicates the liquids which at different p, t values can coexist with solid A and B . To this line belong the p, t lines GQ and HR for the solid phases, which again form a cylindrical surface with EP .

In this way we arrive for the complexes of solid A + liquid at the space included between the liquid-surface, the surface of the solid A , $O_A UQG$ and the cylindrical surfaces $GO_A E$ and $GE PQ$. A similar space includes, at the right, the complexes for solid B + liquid.

Finally, the region of the complexes of solid A + solid B is situated behind the cylindrical surface $GHRQ$ and above the cylindrical surface $NHGM$.

The spaces last described terminate in the figures at the back at an arbitrary temperature and above at an arbitrary pressure. One must suppose that, in reality they continue their course.

The remaining space outside the massive parts constitutes the regions of homogeneous liquids and vapours which pass into each other beyond the critical curve. The other six massive parts represent complexes of two phases, the states of matter forming the complex being represented by two side surfaces.

They further are connected with each other by four cylindrical surfaces on which three lines are always situated representing the systems of three coexisting phases and these cylindrical surfaces intersect each other in one straight line on which is situated the only possible complex of four phases.

If for any system of two substances the figure described were studied completely, it would enable us for each mixture at each temperature and each pressure to read off, of what phases it has been built up and as far as liquid and vapour are concerned it would also show their separate composition.

For the complexes of *two* phases, the relative proportions may also be read off in the figure; for those of *three* or *four* phases it would be necessary to also know the relation of the volumes.

The figure also makes it possible to ascertain what changes a mixture will undergo, when the temperature, pressure¹⁾ or concentration are changed.

Chemistry. — "*Equilibria of phases in the system acetaldehyde + paraldehyde with and without molecular transformation*". By Prof. H. W. BAKHUIS ROOZEBOOM.

(Communicated in the meeting of September 27, 1902).

The character of the equilibria of phases is exclusively determined by the number of independently variable constituents — components — of which the system is built up.

Sometimes this is equal to the number of the different kinds of molecules. It may also be smaller, if there are among the molecules those which may pass into each other as in the case of associating, ionizing or isomeric substances. If these molecular changes proceed more rapidly than the equilibria of the phases, they exercise no influence on them.

Although water, for example, is a mixture of at least two kinds of molecules, its freezing point is quite as sharply defined as that of a single substance.

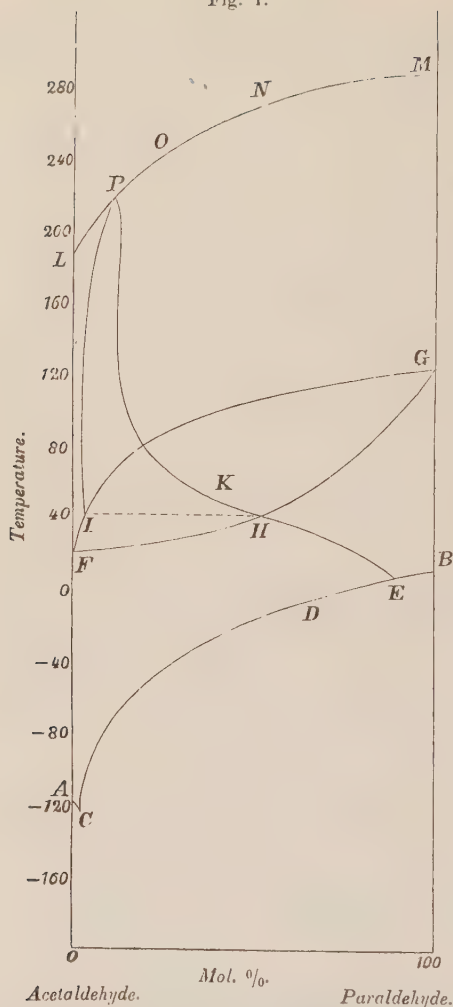
If however, the velocity of the molecular change is small, the system on being treated rapidly will behave like one with more components than it shows if treated more slowly. The effect of this on the phenomena of solidification has already been mentioned by BANCROFT in 1898 and by myself in 1899. So far, however, no suitable example has been found which would enable us to consider

¹⁾ It demonstrates, for instance, in a simple manner that on compressing vapour mixtures with a sufficient amount of *A*, the component *B* first deposits in the solid state in increasing quantity but then again completely disappears at a certain pressure to make room for a liquid phase.

This phenomenon has recently been observed by KUENEN (Phil. Mag. July 1902) with solid CO₂ mixed with C₂H₆.

It must always show itself with the component which in the liquid mixtures is the least volatile: in this case *B*. When however, the liquid-surface has a maximum pressure as in the instance cited by KUENEN, the phenomenon will be noticed with both components. If the surface has a minimum pressure it can only occur with one of the two.

Fig. 1.



at 12°.55 (point *B*). This melting point is lowered by addition of acetaldehyde along to the curve *BEDC*, which continues until the liquid consists almost entirely of acetaldehyde.

With the aid of the apparatus of Prof. KAMERLINGH ONNES¹⁾ the melting point of acetaldehyde was determined at -118°.45 (*A*). The melting point line of acetaldehyde does not extend further than -119°.9 (*C*) where it meets that of the paraldehyde. *C* is therefore a eutectic point,

	Melting point.	% Paraldehyde.
<i>B</i>	+ 12°.55	100
<i>E</i>	+ 6.8	88.1
<i>D</i>	- 4.0	67.6
<i>C</i>	- 119.9	1.4
<i>A</i>	- 118.45	0

¹⁾ LADENBURG gave -120°.

the whole of the equilibria of phases from that point of view.

Such a system has now been investigated in my laboratory by Dr. HOLLMANN of Dorpat. It is the system acetaldehyde + paraldehyde, which has the further advantage of not undergoing molecular transformation except in the presence of a catalyzer and so behaves like a system with two components, whilst it undergoes transformation rapidly enough on addition of a trace of sulphuric acid to appear as a system with only one component. It becomes possible, thus, for the first time to obtain a general insight into the position which equilibria with apparently one component occupy among the systems with two components.

The chief results of the research are the following.

First of all the solidification phenomena of mixtures of acetaldehyde and paraldehyde were investigated. As is well known, paraldehyde in a pure state melts

The boiling points of the mixtures were next determined at a pressure of 1 atmosphere and the composition of the vapour of these boiling mixtures was also determined by means of a special apparatus. The former form the line *FHG*, the latter the line *FIG* of which the following points are the most important:

<i>F</i>	20°.7	boiling point of acetaldehyde
<i>I</i>	41.7	vapour 2.5 % paraldehyde
<i>H</i>	41.7	liquid 53.5 " "
<i>G</i>	123.7	boiling point of paraldehyde.

On account of the great difference in volatility of the two components the liquid- and vapour lines are situated far from each other. The vapour of a boiling mixture is much richer in acetaldehyde than the liquid, for which reason the two are readily separated by fractionation.

In the third place the critical temperatures of the components and of a few mixtures were determined. (Only that of acetaldehyde had been previously found by Prof. VAN DER WAALS to be 184°).

Result:

	Critical temp.	% Paraldehyde.
<i>L</i>	188°	0
<i>P</i>	221°	11.0
<i>O</i>	241°	22.0
<i>N</i>	270°	50.0
<i>M</i>	286°	100.0

These are the relations when there is no transformation of acetaldehyde into paraldehyde, or the reverse.

If, however, a trace of a catalyzer is added, acids in particular, the two molecules can be converted into each other, till the condition of equilibrium corresponding to *p* and *t* has been reached ¹⁾.

It appeared that by these means the boiling point of *all* mixtures came in a very short time to 41°.7 and as this point according to the line *FHG* is situated at 53.5 % of paraldehyde, it represents the relation of equilibrium in the liquid condition at that temperature and 1 atm. pressure. As the corresponding vapour according to point *I* of the vapour line *FIG* only contains 2.5 % of paraldehyde a rational explanation has thus been found of the long-known fact

¹⁾ A little meta-aldehyde is also formed but the quantity remaining in solution is so very trifling that its influence on the system considered may be utterly neglected. It must still be ascertained what place meta-aldehyde occupies in regard to the two forms at high temperatures.

that on distilling paraldehyde with a little sulphuric acid, nearly pure acetaldehyde is collected.

At temperatures below $41^{\circ}.7$, the equilibrium appeared to be displaced along the line HE , which at $6^{\circ}.8$ and 88.1% of paraldehyde meets the melting point line of paraldehyde.

The consequence is that, from whatever mixture we may start, paraldehyde will always crystallise out on adding a trace of sulphuric acid and cooling to $6^{\circ}.8$ and as the transformation of acetaldehyde into paraldehyde proceeds very rapidly even at this temperature, the whole mixture becomes at last a solid mass of paraldehyde. This even proved to be the case when pure acetaldehyde was taken as starting point. On the other hand paraldehyde in the presence of a trace of a catalyzer does not melt at $12^{\circ}.5$ but at $6^{\circ}.5$ owing to partial conversion into acetaldehyde.

We have no knowledge of the equilibrium in the vapour at these low temperatures but something can be said regarding higher temperatures.

The lines FHG and FIG have regard to 1 atm. pressure. Similar lines might however, be determined for a higher pressure and in that manner the displacement of the points H and I with the pressure would be determined. Finally, we should thus arrive at the critical line LM and here the compositions of the vapour and liquid, which indicate the relation of equilibrium, must become the same. It appeared from a series of determinations that the point P at 221° and 11% of paraldehyde is this very point.

At these high temperatures, the equilibrium is also reached after some time without a catalyzer.

It appears from the position of P that the line which gives the composition of the liquid when equilibrium is attained slopes in the beginning very rapidly, with rising temperature, towards the acetaldehyde side of the figure (portion EHK)¹⁾ but afterwards much less rapidly.

The line of equilibrium of the vapour certainly does retrograde, for at 41° the vapour still contains 2.5% of paraldehyde, at 100° less, and at 221° again 11% . In this case the influence of the pressure prevails obviously. As paraldehyde is a triple polymer, the influence of the pressure is very marked.

If we make a representation in space of the whole figure, like the one mentioned in the previous communication, it will be noticed that the equilibria where the possibility of the mutual transformation of acetaldehyde and paraldehyde is admitted, are lines on the surface

¹⁾ The point K has been determined by TURBABA at $50^{\circ}.5$ and 39.4% .

which represents the case that the two components are not subject to transformation.

For this another new representation may be given which considers the matter from a more general point of view.

Taking p , t and x as coordinates, a surface may be constructed which shall represent the equilibrium between the two kinds of molecules in a homogeneous phase, vapour or liquid.



Fig. 2.

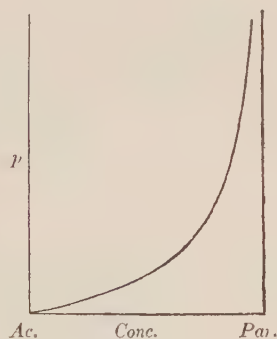


Fig. 3.

The general form of such a surface of equilibrium for the system acet-paraldehyde may be readily deduced from analogy with other known equilibria in the gaseous condition, if one considers that paraldehyde requires heat to pass into acetaldehyde and may be reobtained from the same by compression.

The general course of the equilibrium line at a constant pressure is indicated in fig. 2, that at constant temperature in fig. 3. If we now imagine that on the different points of the t , x -line in a horizontal plane, p , x -lines are erected in vertical planes, we obtain a p , t , x surface of a very peculiar shape which gives the equilibrium relation between acetaldehyde and paraldehyde for every temperature and pressure.

The course may be theoretically calculated for the vapour if the pressure is not too large. With greater pressures and for the liquid state this becomes a difficult matter but the general course remains fairly certain. We might therefore, imagine this equilibrium surface first of all at temperatures higher than those of the critical curve LM . Here, the surface would for some time extend itself undisturbed both vertically and horizontally. At lower temperatures, the surface, on account of its form, must necessarily meet first of all the surface for liquid-vapour; according to the investigation this takes place in the point P . From here to lower temperatures, the

equilibrium surface which was at first continuous will become discontinuous and break up into an equilibrium surface for the vapour state and another for the liquid state.

The lines of intersection of these two surfaces with the surface of two sheets are the lines PI and $PKHE$ in fig. 1. To these must, of course, also be added lines of intersection with the other gas- and liquid surfaces, which have been mentioned in the previous communication.

In this manner, it appears that special equilibria, which occur when transformation between the two components is possible, may be always considered to originate from the intersection of the general space figure for the equilibria of phases with the surface of equilibrium for the molecular equilibria in each phase.

Chemistry. — "*On the action of sulphur on toluene and xylene.*"

By L. ARONSTEIN and A. S. VAN NIEROP. (Communicated by Prof. J. M. VAN BEMMELEN).

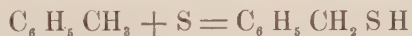
(Communicated in the meeting of September 27, 1902.)

The researches on the molecular weight of sulphur according to the boiling point method of L. ARONSTEIN and S. H. MEIUIZEN¹⁾ showed that this molecular weight was found to agree with the formula S_8 and this in liquids the boiling point of which varied from 45° to 214° . But when toluene and xylene were used as solvents for sulphur the determination of the molecular weight had given values which corresponded with those calculated from formulae ranging between S_7 and S_8 . It was then suspected that this difference might be due to chemical causes. In the following lines we will communicate the results of our efforts to trace those causes.

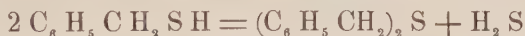
Action of sulphur on toluene. It had already been noticed that on boiling a solution of sulphur in xylene hydrogen sulphide was given off which was shown by means of lead acetate. A similar evolution of hydrogen sulphide was not noticed on boiling sulphur with toluene. As the chemical action of sulphur on toluene at the usually observed boiling point could probably not amount to much, a preliminary experiment was made by heating a solution of sulphur in toluene in sealed tubes at 250° — 300° so as to accelerate the action until on

¹⁾ Proc. Kon. Akad. Wetensch. 1898. First section VI, 3.

cooling the tubes no crystallisation of sulphur took place. In the case of a mixture of 2 grams of sulphur and 10 grams of toluene, this lasted 10 days; in the interval the tubes were repeatedly opened to allow the accumulated hydrogen sulphide to escape. The product obtained was freed from undecomposed toluene by distillation; a preliminary investigation of the residual mass showed with certainty the presence of stilbene, thionessal and probably also of totallyl sulphide. As moreover the contents of the tube had a strong odour of mercaptane it was supposed that the action had taken place in one of the following ways. Firstly, benzyl sulphhydrate might have been formed by a direct addition of sulphur according to the equation:

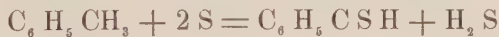


and this on losing hydrogen sulphide according to the equation:

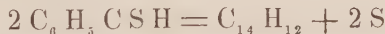


might have yielded benzyl sulphide, which according to FORST ¹⁾ may yield as final products stilbene, totallyl sulphide and thionessal.

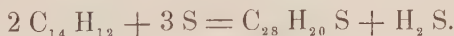
Secondly, the sulphur, according to the equation:



might have yielded thiobenzaldehyde or rather $(\text{C}_6\text{H}_5\text{CSH})_x$, which²⁾ according to the equation:



might have formed stilbene, which then might have formed thionessal according to the equation:



In order to test the accuracy of these theories 4 grams of sulphur were boiled in a reflux apparatus with 150 cc. of toluene for 120 hours, care being taken that any hydrogen sulphide which might have been formed and the non-condensed benzylsulphhydrate were carried off by means of a current of carbon dioxide and passed through an alcoholic solution of lead acetate. Although perceptible quantities of lead sulphide were precipitated during that time not a trace of the well-known yellow lead mercaptide was found. Both the toluene solution and the crystalline mass obtained therefrom were carefully tested for the presence of benzyl sulphhydrate and also of thiobenzaldehyde but notwithstanding the delicate tests for these substances their presence could not be demonstrated. But from the toluene solution we succeeded in isolating stilbene melting at 124° and from this was prepared the characteristic dibromide (m. p. $235-236^\circ$) by

¹⁾ LIEBIG'S Annalen, Band 178. P. 370.

²⁾ BAUMANN & KLETT. Ber. D. Chem. Ges. Band 24, P. 3307.

means of an ethereal solution of bromine. The result justified the belief that the formation of stilbene had taken place in a more simple manner than was formerly supposed, and according to the equation:



The thionessal found in the preliminary experiments might then have originated from the action of sulphur on the stilbene which according to BAUMANN and KLETT readily takes place at 250°. Fresh experiments in which toluene was heated with sulphur for hundreds of hours in sealed tubes at 200° yielded as sole crystallisable product a large quantity of stilbene which was obtained in a perfectly pure condition and of which the bromine addition product with the correct melting point was prepared. In connection with the results of the action of sulphur on xylene to be mentioned presently, we took into consideration the possibility that as a first product not stilbene but dibenzyl might have been formed according to the equation:



and efforts were made to isolate this if possible. As, however, according to the researches of RADISZEWSKI¹⁾, sulphur converts dibenzyl very readily into stilbene and as we had found by special experiments that this already takes place at 200° when a solution of dibenzyl in benzene is heated with sulphur and as we had also proved that this action does *not* take place at a temperature of 140—145° we have heated sulphur with toluene in a sealed tube for eight days at 140°. As sole product we obtained stilbene besides hydrogen sulphide from which fact we are justified in concluding that by the action on the toluene two atoms of hydrogen are directly withdrawn and the two remaining groups are condensed to stilbene.

Action of sulphur on p-xylene. When a solution of sulphur in *p*-xylene is boiled there is a much more perceptible evolution of hydrogen sulphide than on boiling a solution of sulphur in toluene. If, as in the previous experiment with toluene, the gas evolved was removed by means of a current of carbon dioxide and passed through an alcoholic solution of lead acetate 16 milligrams of lead sulphide (equal to 2.1 milligrams of sulphur) were obtained after boiling for an hour and a half. Here again there was no sign of any lead mercaptide; neither did the xylene solution contain a mercaptane as was plainly shown by the fact that no reaction was obtained with mercuric oxide. We next proceeded to heat one gram of sulphur with 30 cc of *p*-xylene in sealed tubes for 120 to 160 hours at 200 to 210° similarly to what was done in the experiment with

¹⁾ Ber. D. Chem. Ges. Band 8. P. 758.

toluene. On opening the tubes much hydrogen sulphide escaped and from the liquid obtained the xylene was distilled off. The residue became quite solid and apparently consisted of sulphur and a crystallised hydrocarbon. To remove the greater part of the sulphur, the hydrocarbon was dissolved in ether which was then distilled off. By recrystallising the residue from alcohol a mass was soon obtained which melted at 81—82°. Two determinations of the molecular weight by the freezing point method with benzene gave, respectively the values 200 and 205. No change took place on heating with hydrogen iodide in sealed tubes and no addition product was obtained on adding an ethereal solution of bromine. The product in fact appeared to be identical with p.p. dimethyldibenzyl $p\text{—CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{.CH}_2\text{C}_6\text{H}_4\text{CH}_3\text{—p.}$ which MORITZ and WOLFFENSTEIN¹⁾ had obtained by the oxidation of *p*-xylene with potassiumpersulphate.

The result which was not analogous to that obtained with toluene caused us to repeat the experiment which now yielded a crystallised product which unlike the first substance was found to consist of a mixture of hydrocarbons. In order to completely eliminate the sulphur the mixture was boiled with solution of sodium sulphite, then dissolved in ether and after distilling off the same, the residue was treated with cold alcohol. The alcoholic solution again contained p.p. dimethyldibenzyl (m. p. 81—82°) as was proved by repeated recrystallisations. The portion insoluble in cold alcohol was solved in boiling alcohol and by repeated recrystallisation a product was obtained which melted at 176—177°, yielded, on adding an ethereal solution of bromine, a bromine product melting at 208° and proved to be identical²⁾ with p.p. dimethylstilbene $p\text{—CH}_3\text{C}_6\text{H}_4\text{CH=CHC}_6\text{H}_4\text{CH}_3\text{—p.}$

In order to find out the cause of the difference in these results a further investigation took place. As far as we were aware, the only difference between the two experiments was that this time the tubes had been repeatedly opened thus causing the removal of the greater part of the hydrogen sulphide. The temperature during the experiment was in both cases the same and constant between 200 and 210°; the heating was also continued for about the same length of time. It was now possible that originally in both cases p.p. dimethylstilbene had been formed. Whilst in the first experiment this substance might have been almost completely reduced to p.p. dimethyldibenzyl by the action of the hydrogen sulphide, this reaction could only have occurred in a limited degree in the second experiment.

1) Ber. D. Chem. Ges. Band 32. P. 2531.

2) GOLDSCHMIDT & HEPP, Ber. D. Chem. Ges. Band 5, P. 1504.

For this investigation a solution of p.p. dimethylstilbene in benzene was saturated with hydrogen sulphide, introduced into tubes the air of which was totally displaced by hydrogen sulphide and after sealing the tubes, the contents were heated for 40 hours at 200°. From these tubes there indeed was obtained, besides unaltered p.p. dimethylstilbene, a product which proved to be identical with p.p. dimethyldibenzyl. This showed that under the given circumstances the expected reaction might have taken place.

On the other hand, dimethyldibenzyl was heated with a solution of sulphur in benzene for 40 hours at 200° and, although it was not yielded in a quantity sufficient to admit of a thorough purification, p.p. dimethylstilbene was obtained; at all events a hydrocarbon melting between 140° and 150° which absorbed bromine and yielded a product melting between 185° and 192°, whereas the melting point of p.p. dimethylstilbene dibromide is situated at 208°. From these experiments it is, therefore, probable that the formation of stilbene is here the primary and that of dibenzyl the secondary reaction, but we here got no certainty about this.

On repeating the experiments on the action of sulphur on *p*-xylene in sealed tubes some of which were opened from time to time unequal proportions of stilbene and dibenzyl were still obtained, but the result of the first experiment (nearly exclusive formation of dibenzyl) was never again obtained.

It should be mentioned here that p.p. dimethylstilbene was often obtained in two different forms. Generally, it was a coarse crystalline powder, but occasionally it consisted of very thin leaflets with a silky lustre and showing a violet-coloured fluorescence. The original form of both was retained after recrystallisation from alcohol. Once we succeeded after a good deal of trouble to convert the coarse granular form by grafting, into the silky condition. The melting point of both forms was identical. On treating them with an ethereal solution of bromine they both gave the same bromine addition product. To see whether this was a case of stereo-isomery, solubility determinations were made of both modifications in absolute alcohol at 25°. In both instances the same solubility value was found, namely 0.21 part per 100 parts of alcohol¹). Notwithstanding the difference in appearance which was also retained in these solubility experiments, a stereo-isomery has thereby been rendered very improbable.

¹) ELBS (Journal f. Pract. Chemie. Neue Folge Band 39. P. 299 and Band 47. P. 46) gives the solubility of p.p. dimethylstilbene in alcohol at the ordinary temperature as 0.76 per 100.

Action of sulphur on m-xylene. Sulphur boiled with *m*-xylene not only gave a much smaller evolution of hydrogen sulphide than in the case of *p*-xylene but the amount was even less than that obtained on boiling sulphur with toluene. *m*-Xylene which had been boiled for a considerable time with sulphur was quite as free from mercaptane as the similarly treated toluene and *p*-xylene.

We now proceeded to heat sulphur and *m*-xylene in sealed tubes at 200°. After the heating had lasted for 70 hours, the sulphur had totally disappeared and the tubes could be opened. Streams of hydrogen sulphide escaped. From the liquid obtained the xylene was distilled off and the liquid non-crystallisable residue was freed from sulphur by boiling with solution of sodium sulphide. As it was not improbable that both m.m. dimethylbenzyl and dimethylstilbene might have been formed (to judge from the behaviour of *p*-xylene) and as the first named substance is, according to VOLLRATH¹⁾ and MORITZ and WOLFFENSTEIN²⁾, a liquid and the unknown m.m. dimethylstilbene probably a crystallisable substance it was tried (although in vain) to effect a separation of these two substances by heating in a current of steam, by fractional distillation at ordinary pressure and also by solvents. The suspected presence of a stilbene in that liquid was, however, soon proved when bromine was added to its ethereal solution and the whole placed in a freezing mixture. A bromine-addition product now crystallised in abundance. The addition of bromine was continued until a small excess was present. The crystallised product after being recrystallised twice from xylene had a constant melting point of 167—168°. A bromine determination according to CARIUS gave 44.02 % of bromine, the calculated quantity for dimethylstilbene dibromide being 43.50 %.

The dibromide was used to prepare the hydrocarbon itself. For this purpose it was dissolved in xylene and boiled with molecular silver or sodium wire for 6 hours in a reflex apparatus. From the xylene solution obtained the xylene was removed by distillation; the residual liquid crystallised on cooling and the crystalline mass could be readily purified by recrystallisation from alcohol. The substance is very difficult to burn; the combustion only succeeded by intimately mixing it with lead chromate and potassium bichromate. The elementary analysis gave the following result:

Found	C. 92.19 %	H 7.91 %
Calculated for C ₁₆ H ₁₆	C. 92.30 %	H 7.70 %

¹⁾ Zeitschr. f. Chemie 1866. P. 489.

²⁾ Ber. D. Chem. Ges. Band 32. P. 2532.

The melting point was constant at 55—56°.

That the obtained hydrocarbon was really m.m. dimethylstilbene was proved by adding bromine to its ethereal solution which immediately yielded crystals of the dibromide with the previously found constant melting point of 167—168°.

The ethereal liquid from which the dimethylstilbene bromide was precipitated, contained, of course, free bromine from which it was freed by treatment with aqueous potash. After distilling off the ether, the liquid was submitted to fractional distillation when hydrogen bromide was evolved owing to the presence of brominated products. The hydrogen bromide present in the distillate was removed by treatment with aqueous potash and the liquid distilled once more. When it appeared that this distillate, passing over between 298° and 302° was not yet free from bromine it was dissolved in toluene and boiled for three hours with sodium wire which completely removed the bromine. The liquid then showed a constant boiling point of 298°. On analysis was found:

C 91.38% H. 8.64%

Calculated for $C_{16}H_{18}$ C 91.43% H. 8.57%.

Two determinations of the molecular weight by means of the lowering of the freezing point in benzene gave 201 and 199; calculated 210°. All data agree with those of VOLLRATH and those of MORITZ and WOLFFENSTEIN for m.m. dimethyldibenzyl. Only the boiling point was found to be two degrees higher.

From this it, therefore, appears that *m*-xylene on treatment with sulphur yields stilbene as well as dibenzyl as decomposition products.

To ascertain whether stilbene was here also the first product, m.m. dimethyldibenzyl was submitted to the action of sulphur by boiling it with this in a reflex apparatus. The product of the reaction dissolved in ether and treated with bromine did not yield a trace of the characteristic m.m. dimethylstilbene dibromide. This substance could not even be recognised by means of the microscope.

From this we think we may come to the conclusion that during the action of sulphur on *m*-xylene the first product is most probably stilbene and that dibenzyl is a secondary product formed by the reducing action of hydrogen sulphide.

The results of this research are, as we believe, a confirmation of the opinion expressed by ARONSTEIN and MEIHZEN in their treatise on the molecular weight of sulphur. A trifling action of the sulphur on toluene and xylene must cause a derivation of the molecular weight in the direction previously found. One mol. of sulphur causes the formation of 8 mols. of hydrogen sulphide and 4 mols of stilbene.

Although hydrogen sulphide is volatile and most of it escapes during the boiling, the increase of the number of molecules formed during that action (however small this may be) is large enough to account for the observed difference. The fact that the deviation has been found larger in the case of toluene than with *m*-xylene as solvent is also in agreement with the observed fact that more hydrogen sulphide is evolved in the first than in the second case.

Our research on the action of sulphur on *p*-xylene was not conducted merely with the idea of confirming the researches of ARONSTEIN and MEIUIZEN (we were not quite sure whether the *m*-xylene then used had been completely free from *p*-xylene) but also to throw more light on the mechanism of the process and particularly on the question of the primary formation of stilbene and the secondary formation of dibenzyl.

Chemical Laboratory of the Polytechnical School.

DELFT, September 1902.

Physiology of Plants. — "*Investigations of Glucosides in connection with the Internal Mutation of plants,*" by MR. TH. WEEVERS.
(Communicated by Prof. C. A. LOBRY DE BRUYN).

(Communicated in the Meeting of 27 September 1902.)

The purpose I had in view in this investigation was to trace for some plants, whether the amount of glucosides remains unchanged during the development or not; and to investigate in the latter case by what conditions these changes are determined.

At the same time the manner in which those changes took place formed another subject for study: whether glucosides were transported as such, or whether a decomposition could be stated, and in the latter case what were the components in which this took place.

Salix species and *Aesculus hippocastanum* L. were especially used for the investigations; *Gaultheria procumbens* L. and *Fagus sylvatica* were also submitted to a prefatory study.

The glucosides to be mentioned here are salicine for the *Salix* species, gaultherine for *Gaultheria* and *Fagus*, aesculine and moreover some glucosides not yet chemically determined for *Aesculus hippocastanum*.

As for salicine the quantitative valuations were made as follows. The salicine was entirely extracted by boiling water from the parts to be examined and the extract treated with basic lead acetate. The

surplus was removed by dinatriumphosphate and the liquid then obtained reduced to a definite volume. In this two estimations of sugar were made, one before, the other after allowing emulsine to work in upon it for 48 hours. Prefatory experiments with pure salicine had proved that in this way it was completely decomposed: the increase of the reduction after inversion was to be attributed only to the glucose formed of salicine.¹⁾

From this increase of the glucose the quality of the salicine could then be calculated.

This same method was followed in order to state the salicine in various parts of the plant; then however, after inversion the liquid was extracted with ether, so that saligenine might enter into it. This substance is easily recognised by the physic qualities of its crystals and by the substitute of bromine obtainable with brominewater and moreover by its salt of copper. The efforts to point out salicine in the tissue itself were unsuccessful; the method formerly used by THEORIN²⁾, namely that of adding concentrated sulphuric acid, proved impracticable, as it during the produced erroneous results.

For the above mentioned *Salix* species salicine is found in the bark of the branches, but not in the wood; young buds are rich in it, likewise the assimilating leaves. It appears in young ovaries but disappears during the process of ripening.

Although an inverting enzyme was not to be extracted, it proved necessary to kill the parts immediately in boiling water, otherwise considerable alterations in the quantity of salicine presented themselves. Thus e.g. after slow drying 25 pCt. disappeared out of the bark.

The following series of determinations for the purpose of investigating the quantity of salicine during the budding period, was made with *one* specimen to exclude individual differences.

The total quantity in various successive stages was calculated by taking a branch with a definite number of sidebuds as object. The weight of the different parts of this branch together with the procentic values of the quantity of salicine in corresponding parts of the same object in the successive stages gave the total quantity of salicine of this branch in those stages³⁾.

¹⁾ Before inversion a solution of salicine does not reduce even with boiling; neither does saligenine formed by means of inversion at the same time as glucose.

²⁾ See Theorin Öfersigt af Kongl Vetenskaps. Akademiens Förhandlingar 1884. No. 5. Concentrated H_2SO_4 gives with salicine a coloring of red.

³⁾ In corresponding parts of *one* object was an equal quantity.

Under observation were only branches without genitals; those with catkins gave a different result¹⁾.

Branches of $1\frac{1}{2}$ —4 mM. diameter (wood and bark together).

March 24th 3.2 pCt. ²⁾

April 17th 2 "

May 21st 0.4 "

Branch of 4—8 mM. diameter (only bark; hence the quantity is higher).

March 24th 4.1 pCt.

April 17th 2.8 "

May 21st 2.1 "

For *Salix Helix* L. the figures for the bark of branches were

March 24th 4.4 pCt.

April 17th 2.7 "

The quantity of glucose is a little variable; however, it does not rise above 0.5 pCt.; the quantity of fecula diminishes when budding from 9.5 pCt. to 6 pCt.

In the young buds of *Salix purpurea* there is before the budding 4.4 pCt. and of *Salix Helix* 6.2 pCt. During the budding this quantity decreases greatly, disappears even for *S. purpurea* entirely (17 April) but rises again quickly, when assimilation begins, to 3.7 pCt. in leaves and 3 pCt. in young shoots (21 May).

Of the absolute quantity of salicine in a branch with 300 buds

± 36 pCt. disappeared from 24 March—17 April

± 18 " " " 17 March—21 May,

the assimilation, begun already before May 21, having given rise to new salicine.

Experiments with branches placed in the dark in water³⁾ showed the following:

After the roots have been formed, a number of long etiolated shoots bud forth, consuming by their development besides the fecula also a great quantity of the salicine in the bark (± 70 pCt.).

At first the young shoots contain a great quantity 7.2 pCt., this, however, keeps on decreasing; the absolute quantity calculated for 100 young shoots also diminishes:

for 100 young shoots long 18 mM. there is 28 mG. salicine

" " " " " 125 " " " 15 " "

¹⁾ The quantity of salicine is at the same instant lower in branches with catkins than in those without; the salicine diminishes more quickly.

²⁾ These procentic values are calculated for dry weight.

³⁾ These were branches of 6—10 mM. diameter, the young shoots coming from sleeping buds.

These quantities are small compared to the entire quantity consumed \pm 330 mG. for 100 young shoots.

When the young buds were budding forth saligenine was found in them, the branches were immediately killed in boiling water, the extract after cooling down extracted with ether; so all influence of enzyme could be excluded. It becomes very probable that the salicine is analysed before the consumption, on account of saligenine being found; the quantity, however, is so small that if really the analysis of salicine were to take place as indicated, and a decomposition to precede the consumption, saligenine can only be an intermediate stage. Either the aromatic half disappears as such, or another aromatic substance must be the definite product of the decomposition.

In the young leaves developing normally, salicine soon makes its appearance again after having disappeared for a moment; we can expect that this increase is connected with and due to the assimilation, as etiolated shoots do not show it. In order to state whether the leaves were really the place of a new formation and the light really had a part in it, the quantity of salicine before and after darkening was compared.

The quantity in the leaves was determined in the evening after sunset and in the morning before sunrise (*one* specimen). Likewise in the evening leaves were halved, one half with midrib left on the plant, the other half analysed. The following morning the remaining half was cut off from the midrib and also analysed¹⁾. Provided that a sufficient number, 100 or 200 leaves were halved, a comparison could very well be made.

For a small-leaved specimen a 100 leaves

8 P. M.	7 Aug.	47.5 mG.	glucose	87.2 mG.	salicine
4 A. M.	8 "	27.4 "	"	60.2 "	"

For a big-leaved specimen a 100 leaves

8 P. M.	7 Aug.	80 mG.	glucose	177.7 mG.	salicine.
4 A. M.	8 "	31.9 "	"	142.7 "	"

So in both cases we see a decrease during an 8 hours' summer night of respectively 30 and 20 % of the salicine in the leaf in the evening.

For experiments with entire leaves of *one* specimen :

8 P. M.	7 Aug.	4.6 %	salicine.
4 A. M.	8 "	3.2 %	"
8 A. M.	8 "	4.6 %	"

¹⁾ See Lotsy. Mededeelingen 's Lands Plantentuin XXXVI.

Thus here too a decrease of 30 % during the night followed up by an equal increase on the following day. If branches on the plant are enveloped in black waxed paper the decrease amounts after 48 hours only to 35 %, no great difference with that of 8 hours; increase, however, did not take place, so light proves to be a necessary factor. The experiments of etiolating told the same.

If this quantity of salicine disappearing from the leaves was removed to the bark, an increase would have to be observed there. This was indeed the case, for branches rich in leaves the increase of the quantity of salicine of the bark amounted in *one* night to 2.5 %; for branches with few leaves to 1.1 %.

From the etherextract prepared in the above described manner, of the parts of *Salix purpurea* still another substance could be isolated by means of subliming. According to the micro-chemic qualities this was a substance resembling phenol and qualified by its compound of lead and of lime, besides reaction with tetrachloorchinon as an ortho-derivate¹⁾. The substance did not show Aldehydreactions. The further micro-chemical qualities corresponded to those of the simplest ortho-phenol, catechol. After a repeated crystallisation out of benzol the melting-point proved to be 104°. Elementary analysis and determination of molecular weight confirmed the fact, that it was catechol.

As the material which furnished the substance was quickly killed both in boiling water and in boiling alcohol and the etherextract already showed the crystals before sublimation, influence of enzym²⁾ is not probable and formation out of resin is not possible.

Treatment with ferrichloride followed by additon of natrium hydrocarbonate also furnished in the tissue the reaction of catechol. The red colour was clearly visible in the unopened cells of the sections of the bark, young etiolated shoots showed them faintly, older ones more. Catechol is like salicine only to be found in the bark³⁾.

The supposition was aroused that catechol might be the aromatic substance, remaining there as definite product of decomposition of the salicine. In order to test the accuracy of this supposition, an investigation had to be made whether the quantity of catechol of the parts of *Salix purpurea* were varying.

For a quantitative determination of the catechol the method of

1) According to an investigation of Prof. H. BEHRENS which will shortly appear, communicated to me by Miss GRUTTERINK.

2) The black colour of the dying leaves is caused by the influence of a "tyrosinase" on catechol.

3) Catechol was also obtained out of *Salix Helix* L., *S. babylonica* L., *S. vitellina* L., *Populus alba* L., *P. monilifera* Ait, sometimes only very little.

DEGENER (Journal f. Prakt. Chemie 1879) could not be used on account of a flavon-like colouring matter not closer examined, and also precipitated by a basic leadacetate. So the method of Prof. BEHRENS to determine Indigo was followed. The sublimate of a solution of catechol of a known strength in absolute alcohol was compared with that of the alcoholic solution of the remainder of the ether evaporated dry. Now it was examined how much this liquid had to be diluted to obtain an equivalent sublimate. The sublimation was performed by means of the brass table described by Prof. WIJSMAN. Under certain precautions the determination could be accurately made to milligrammes.

The quantity of catechol of the leaves was in the evening	0.6 pCt.	} with one specimen
" " " " " " " " " " morning	0.1 " "	
" " " " " " bark " " " evening	0.6 " "	} with the same specimen.
" " " " " " " " " morning	0.4 " "	

So the quantity of the catechol here proved to change in reverse order as that of the salicine. In the leaves the salicine diminishes in the night, the catechol increases, and in the bark the catechol diminishes and the salicine increases. Is there any connection between the extent of these changes?

For that purpose for one and the same object catechol was determined as well as salicine.

200 halves of leaves	8 P. M.	225 mGr. salicine	(4.5%)	± 32 mG. catechol	(0.65%)
" " " " "	4 A. M.	162 " "	(3.3%)	± 52 " "	(1.05%)

So 63 mG. salicine less, 20 mG. catechol more.

The proportion of these values, given the degree of accuracy of the determination of catechol, pretty well agrees with the proportion of the molecular weights.

A comparison was also made of the change in salicine with that in catechol for leaves budding forth in the dark.

17 Gr. bark before budding	351 mGr. salicine	36 mGr. catechol
17 " " after " "	232 " "	55 " "
budding etiolated shoots	55 " "	4 " "

(a great increase in the bark, in the young shoots only a small part of the catechol thus formed to be found) 64 mG. salicine was used, 23 mGr. catechol was formed.

These two values stand in the ratio of 36 to 100, the molecular weights in that of 38 to 100.

So it is very natural to assume here a decomposition of the salicine into sugar and catechol with saligenine as intermediate stage (see

above). For this then a CH_2 group out of the lateral chain would have to be decomposed, as saligenine is orthoöxybenzylalcohol and catechol is the orthodiphenol.

Corresponding to this the quantity of catechol of the bark is large in May (1.1 pCt.), a greater part of the salicine then having disappeared, much lower in July (0.3 pCt.) when the loss has been repaired ¹⁾. Where now has the decomposition taken place?

PFEFFER says Kap. VIII, Pflanzenphysiologie 2^e Auflage: „vielleicht dienen die esterartigen Verbindungen der Kohlenhydrate mit Phenolkörpern zur Herstellung von schwer diosmirende Verbindungen bei deren Zerspaltung im allgemeinen der Phenolkörper in der Zelle intact verbleibt, um fernerhin wieder zur Bindung von Zucker benutzt zu werden.“

The facts are excellently explained in the following way:

The decomposition of the salicine takes place in every cell, the glucose is conveyed in the direction of the green parts, the catechol remains in the cell and binds glucose, coming from cells situated closer to the bark, to salicine.

Glucose is transportmatter and salicine is transitory reservematter.

The glucose being consumed in young parts in greater quantities than its supply is, catechol must be found, but only so much as corresponds to the decrease of the absolute quantity of salicine.

100 young shoots 18 m.M. long 28 m.G. salicine, traces of catechol.

100 " " 85 m.M. " 21,6 m.G. " 2 m.G. "

6.4 m.G. salicine corresponds when calculated to 2,5 m.G. catechol, when observed to 2 m.G.

This correspondence adds great strength to the hypothesis. ²⁾

In the bark the loss of consumed glucose is not repaired, so catechol increases greatly.

As for Aesculus, here it was especially the germination which was studied. The glucosides found in the ripe seedlings being not yet chemically determined, it was only necessary to base the method of the quantitative definition on the quantity of sugar formed by inversion. I had to trace whether the quantity of sugar bound in glucoside decreased during the germination.

To this end the seedlings were ground and extracted with methyl-alcohol, of this extract the alcohol was evaporated, and the watery liquid

¹⁾ I here mean the quantity in the bark of thicker leafless branches where no difference between night and day is observed.

²⁾ Also the facts observed at the change of night and day can be excellently explained in this way.

extracted with ether to get rid of oil and resin. The extracted liquid served as definition of the reduction *before* and *after* inversion by boiling it for 2 hours with HCl ¹⁾.

From the difference of this reduction the quantity of reducing sugar originating from the glucoside could be calculated; it amounted to 13 pCt.

During the germination this quantity decreased in cotyledons by 60 or 70 pCt. Fecula and albumen by 70 or 80 pCt. The germinating plants contained only 1 or 2 pCt. of glucose bound in the shape of glucoside, the consumption of the glucosided sugar during the germination could be regarded as proved by the 70 pCt. decrease of the absolute quantity.

The localisation of aesculine was observed by fluorescence of its watery solution, to be seen when there are not too few sections. Aesculine was to be found in ungerminated seeds only sporadically in the plumule; when germinating it appears in greater quantity in the stalks of cotyledons, not in the cotyledons themselves. Stalk and hypocotyledon internodium contain aesculine when germinating in the dark as well as in the light, so light is not necessary for the formation.

The stalks of the leaves show the aesculine only when developing in the light and not in the dark; this seems to point to the fact, that the aesculine of the normal germinating plant originates from two sources: that it is formed for the greater part by reforming of substances out of the cotyledons and side by side with this, that it is prepared independently in the stalks of the leaves from substances assimilated by the leaves. Experiments with full-grown plants, in the light and in the dark, with coloured and with normal leaves made this the more propable, but full certainty can only be given by means of later quantitative definitions.

Studies on *Gaultheria procumbens* showed what changes took place in the quantity of the gaultherine, the investigations have however not yet been brought to an end. The method of quantitative definitions was founded on the observation of the quantity of methylsalicylate which could be formed out of it. This was redistilled with vapour out of the parts, caught in alcoholic potash and saponificated with it. The kaliumsalicylate formed in this way was determined according to the method of MESSINGER and VORTMANN ²⁾. For smaller quantities the colorimetric method of determination was used with FeCl_3 .

1) After inversion and neutralisation the liquid was treated with leadacetate.

2) MESSINGER and VORTMAN, Zeitschrift f. Anal. Chem. 38 bl. 292.

Ber. d. deutschen chem. Gesellschaft. Berlin. Bd. 22. 2313.

With *Fagus sylvatica* where TAILLEUR¹⁾ found methylsalicylate only in the germinating plant, the latter method showed that it was also present in the full-grown plant. Methylsalicylate is to be found sporadically in the buds of the beech shortly before budding, during that process it is found in the young leaves and shoots as well as in the branches of the preceding year. Young long branches are richest in it, 0.02 pCt. As soon as the leaves have unfolded, this substance begins to disappear again and is nowhere to be found in a week's time.

Further particulars to be looked for in the dissertation to appear shortly.

Physics. — *"Some observations on the course of the molecular transformation."* By Prof. J. D. VAN DER WAALS.

As is well known, acetic acid may be considered as a mixture of simple and double molecules and we find a decreasing number of double molecules when we investigate the saturated vapour of this substance at increasing temperature. The same applies also to NO_2 . We are apt to conclude from these two best known instances of molecular transformation that this course is the only one that is possible. We may, however, easily convince ourselves that also the opposite course may occur, and it appears to me that we may conclude from figure (1) of the communication of Prof. H. W. BAKHUIS ROOZEBOOM in the Proceedings of the previous session, that for the transformation of acetaldehyde and paraldehyde this opposite course perhaps occurs.

Let us take the equation for the molecular transformation, as it occurs Cont. II, pag. 29, namely:

$$\log \frac{(v-b)x}{(1-x)^2} = \frac{2(E_1 - E_2)}{R_1 T} + 1 - \frac{2(H_1 - H_2)}{R_1}$$

The quantity $1-x$ of this equation represents the quantity of the substance expressed in grams which occurs in the form of simple molecules, x therefore that which occurs in the form of double molecules. If molecules were formed consisting of n simple molecules, the equation would be modified into the following one:

$$\log \frac{(v-b)^{n-1}x}{(1-x)^n} = \frac{A}{T} + B.$$

It is true that we only find the equation in this simple shape if

¹⁾ TAILLEUR, Comptes Rendus A. Sc. Tome 132 p. 1235.

we make suppositions concerning the quantities a and b , which can only be satisfied if the multiple molecules may be considered to be mere complexes of simple molecules, which can be formed without further radical modifications in the structure of the molecules themselves. But as I will apply the given formula only in the case of saturated vapour at a pressure which is not very high, in which case the influence of the quantities a and b may be neglected, we may consider it to be sufficiently accurate for our aim.

We may deduce from it:

$$(n-1) \frac{dv}{v dT} + \frac{dx}{dT} \left(\frac{1}{x} + \frac{n}{1-x} \right) = - \frac{A}{T^2}.$$

For saturated vapour at a pressure which is not too high, we have:

$$pv = R_1 T \left(1 - \frac{n-1}{n} x \right),$$

from which follows:

$$\frac{dp}{p dT} + \frac{dv}{v dT} = \frac{1}{T} - \frac{\frac{n-1}{n} \frac{dx}{dT}}{1 - \frac{n-1}{n} x}.$$

If we substitute for $\frac{1}{v} \frac{dv}{dT}$ the value found above, we get the equation:

$$T \frac{dx}{dT} \frac{1}{x(1-x)(1 - \frac{n-1}{n} x)} = (n-1) \left(\frac{T}{p} \frac{dp}{dT} - 1 \right) - \frac{A}{T}.$$

Whether the number of multiple molecules in the saturated vapour increases or decreases with the temperature, depends therefore on the fact whether the value of the expression:

$$(n-1) \left(\frac{T}{p} \frac{dp}{dT} - 1 \right)$$

is more or less than $\frac{A}{T}$.

For a normal substance $\frac{T}{p} \frac{dp}{dT}$ is approximately equal to $7 \frac{T_{cr}}{T}$.

For a substance in which molecular transformation takes place, the factor 7 is to be modified and this factor will even vary more or less with the temperature. But if a perfectly accurate numeric determination is not required, and if we only ask: Can both ways in which x may be thought to vary with the temperature occur? then we may state what follows:

"When the heat developed by the combination of n simple molecules to a complex one is so great, that it far exceeds the quantity $(n-1) 7 T_{cr}$ — as is the case for acetic acid — then the saturated vapour will at higher temperature be associated in a lower degree. If on the other hand that quantity of heat is much smaller than $(n-1) 7 T_{cr}$ then the reverse will take place."

When we proceed to saturated vapours of greater density and when we approach the critical temperature, then this difference in the course will no longer exist.

If we consider in the equation :

$$(n-1) \frac{T}{v-b} \frac{dv}{dT} + T \left(\frac{1}{x} + \frac{n}{1-x} \right) \frac{dx}{dT} = - \frac{A}{T}$$

the value of $-\frac{T}{v-b} \frac{dv}{dT}$ for the saturated vapour at all temperatures between 0 and T_{cr} , we see that this quantity has a minimum value for a certain value of T . For very low temperatures it may be equated to $f \frac{T_{cr}}{T}$ and for the absolute zero it is therefore infinite.

But also for $T=T_{cr}$ it will be infinite, for $-\frac{dv}{dT}$ is infinite in the critical point. The value of T for which this minimum value occurs, would for normal substances be the same fraction of T_{cr} . For substances with molecular transformation we find a different value for this fraction. It may be calculated for many substances from the experiments of SIDNEY YOUNG at least approximately.

Above the temperature for which $-\frac{T}{v-b} \frac{dv}{dT} = \frac{A}{T}$ for acetic acid also $\frac{dx}{dT}$ is again positive. For substances which behave as acetic acid therefore a minimum value of x occurs. The fig. (1) of BAKHUIS ROOZEBOOM presents in fact such a minimum for paraldehyde, and from this would follow, that this transformation is of the same type as that of acetic acid. Yet it seems possible to me that an accurate direct investigation would prove this minimum not to exist. If it really exists, then it will probably occur at a much higher value of T .

But even if this transformation would also prove to be of the same type as that of acetic acid, yet it seems not superfluous to me to point out, that also the other type may possibly occur. The abnormality of substances as the alcohols, water, etc. is ascribed to a possible molecular transformation, and yet the saturated vapour

of these substances appears to follow the laws of the perfect gases the more accurately as the temperature at which it is investigated is lower. So the density of saturated vapour of water at 100° , appears to be $2\frac{1}{2}$ pCt. higher than would follow from the application of the laws for perfect gases; whereas the saturated vapour of water at ordinary temperature presents a density which does not deviate noticeably from that, which follows from the laws of BOYLE and GAY-LUSSAC. If for molecular transformation the type of acetic acid were the only one which could occur in nature, then the supposition that water is also subjected to this transformation would involve that the deviation would be found to increase when the temperature is lowered. It is highly probable that the deviation of $2\frac{1}{2}$ pCt. of saturated vapour of water at 100° , which cannot be accounted for by the ordinary deviation from the laws of BOYLE and GAY-LUSSAC which also normal substances present, must be ascribed to the presence of more complex molecules; but at the same time we must then assume, that the heat of transformation lies below the limit which we have indicated above.

The equation which we have used here, is taken from Cont. II, p. 29 and there it had been obtained by the direct application of the principle of equilibrium, according to which a given quantity of matter at a given temperature in a given volume will arrange itself in such a way that the free energy is a minimum. It is therefore that we had to take a fixed quantity of the substance, e. g. a unit of weight, which might be divided into $1-x$ grams simple, and x grams double molecules. When x varies, the total quantity of the substance remains constant.

We may, however, also consider a mixture, consisting of a number of $1-x$ simple and x multiple molecules and then we may apply the thesis that, when equilibrium is established the thermodynamic potential for a molecular quantity of the multiple molecules must be n times greater than that for the simple molecules. The linear function of x , however, which in other cases may be omitted, must in this case of course be preserved. If we then put:

$\zeta = MRT \{ \mu + (1-x) l(1-x) + x l x \} + T \{ \alpha(1-x) + \beta x \} + \gamma(1-x) + \delta x$
then we have:

$$\zeta - x \frac{\partial \zeta}{\partial x_{pT}} = MRT \{ \mu - x \mu'_x + l(1-x) \} + \alpha T + \gamma,$$

$$\text{and } \zeta + (1-x) \frac{\partial \zeta}{\partial x_{pT}} = MRT \{ \mu + (1-x) \mu'_x + l x \} + \beta T + \delta.$$

From $\zeta + (1-x) \frac{\partial \zeta}{\partial x_{pT}} = n \left\{ \zeta - x \frac{\partial \zeta}{\partial x_{pT}} \right\}$ we deduce:

$$\log \frac{x}{(1-x)^n} = (n-1) \{ \mu - x\mu'_x \} - \mu'_x + B + \frac{A}{T}.$$

This last equation yields the results we have obtained, in a still simpler way than that which we have made use of originally. It has moreover the advantage, that the usual signification of x and μ , as it is established in the theory of a binary system, may be kept unchanged.

Reactions like that of acetaldehyde and paraldehyde, reactions which we can bring about at pleasure by means of a catalyzer and in which the composition may be determined experimentally are of course of the highest importance for the investigation of the course of the molecular transformation. For reactions as that of acetic acid the density is the only criterion for the degree of the transformation; and this criterion fails as soon as we work in circumstances in which the deviations from the laws for the perfect gases are considerable. The experimental investigation will therefore not be able to prove the occurrence of a minimum in the number of the double molecules in the saturated vapour of acetic acid. At the temperature at which the theory predicts that minimum and which lies probably between $0.8 T_{cr}$ and $0.9 T_{cr}$, the density of the saturated vapour is already so great that it is nearly impossible to deduce reliable conclusions concerning the course of the transformation.

Physics. — "*Critical phenomena in partially miscible liquids.*" By Prof. J. D. VAN DER WAALS.

I have read with great interest the communication of Prof. KUENEN under the above title, which occurs in the Proceedings of the previous session, and it induces me to draw attention to the following considerations.

In my paper of March 25th 1899 I started from the thought, that the series of plaitpoints, which may occur at different temperatures, whether we arrange them to a plaitpoint curve or assign a place to them in the x, v plane, must form one or more continuous curves — of course continuous in the mathematical sense.

When therefore the experiment yielded, e.g. for ethane and ethyl-alcohol two separate plaitpoint curves, I have connected them by means of a theoretical part.

If we wish to connect the two pieces of curves found to one curve, we may perform this in two simple ways. In the first place we may connect them in such a way that the curve is con-

tinuous also as to its direction. In the second place we may, between the ends of the pieces which are experimentally determined, trace a curve which presents in those ends abrupt changes of direction and which has about the same course as the three-phase pressure, though it lies everywhere lower than that pressure.

I then thought that the two pieces of the plaitpoint curve were to be connected in the first manner. The experiment had shown that the peculiarities which must then occur, namely the existence of a minimum and of a maximum temperature, were possible and really occurred in nature; at any rate the minimum temperature. The peculiarity, on the other hand, which occurs, if we make the connection in the second manner, namely the abrupt change of the direction, was never observed.

Now when we have made a choice and when we wish to examine its meaning, all conclusions must of course be in accordance with the choice we have made. Here I will mention the following conclusions from the first way of bringing about the connection: 1st. A mixture with minimum critical temperature exists. 2nd. A mixture with maximum critical temperature exists. 3rd. Plaitpoints occur outside the borders of the three-phase temperature, which cannot be observed, as they lie above the empirical ψ -surface.

In this case a plait must necessarily at a certain temperature be separated from the principal plait, which at higher temperature (the maximum critical temperature) has contracted to one point. In short then the phenomenon quite corresponds to the description I have given Cont. II, p. 187. If therefore KUENEN accepts the way in which the connection of the two pieces of the plaitpoint curve he has determined experimentally, is brought about, then I cannot but consider it to be inconsistent, if he raises objections to the interpretation.

But more important is the question whether the choice we have made is the right one; whether, therefore, the connection between the two pieces of the curve should not rather be brought about with two abrupt changes in the direction. This has at the same time the following meaning. Is the plaitpoint the course of which is indicated by the theoretic curve, perhaps quite another plaitpoint as that whose course is indicated by the experimental curve? Now I read in the paper of KUENEN p. 321 that he has obtained the figure I have originally given, with the aid of other curves. But I think that this must be understood in such a way that he has succeeded in pointing out, that the two ends of the experimental branches may be connected. The way in which the connection must be established can here, after my opinion, not be decided. I have already doubted some time as to

this question. The first way of connecting requires that as well a mixture with a maximum, as a mixture with a minimum critical temperature occurs. And though I expressed in my paper of 1899 the expectation, that it would be possible to account for this, yet I must acknowledge, that a further investigation has made me consider the occurrence of a maximum critical temperature more and more improbable.

After my opinion the question is decided by that part of the plaitpoint curve KUENEN has determined experimentally, which starts at the critical point of methylalcohol and which indicates the course of a plaitpoint belonging to a plait which has its summit towards the side of the small volumes. The fact that $\frac{dp}{dT}$ is negative or at any

rate smaller than $\left(\frac{\partial p}{\partial T}\right)_v$ quite agrees with the circumstance, that

$\left(\frac{d^2 v}{dx^2}\right)$ is positive.

If this plait had its summit on the side of the large volumes, then it would be possible to explain the course also for the case of ethane and methylalcohol by admitting the existence of a maximum and a minimum T_{cr} . As this is however not the case it seems to me that we cannot but assume with KUENEN, that the theoretical part of the plaitpoint curve indicates the course of a point, drawn i. a. by KORTEWEG (Archives Néerl. XXIV, p. 305, fig. 12) and which belongs to a sideplait if we trace the connodal curve of the sideplait also in the unstable region. The discontinuity in the direction of the curve ensues then from the fact that the theoretic part represents the course of another plaitpoint than the experimental part.

If we return to the case of ethane and methylalcohol then we must admit that above T_B the spinodal curve possesses a protuberance towards the side of the small volumes, accompanied by a new connodal curve, which if we trace it also in the unstable region, presents a new plaitpoint. Or, what comes to the same: the existing plaitpoint splits up into two plaitpoints. This second plaitpoint lies on the side of ethane and in the beginning it will move with great velocity. At higher values of T the sideplait extends and in consequence thereof that part of the principal plait which has a plaitpoint on the side of ethane contracts. At the moment that that part would vanish the second plaitpoint has coincided with the plaitpoint which is indicated by the point A (see fig. (1) of p. 319). This description differs in details from that of KUENEN, but a great number of figures would be required

in order to show this difference clearly, but then also in order to bring us into agreement.

For the case of ethane and methylalcohol the theoretical plaitpoint belonging to the sideplait of the side of alcohol coincides at T_A (see fig. 2, p. 326) with the practical plaitpoint of the side of ethane. At lower value of T it is displaced in the x, v -plane towards the side of alcohol and when the temperature continues to decrease it approaches asymptotically to the plaitpoint with which it forms a "système double hétérogène" (after the terminology of KORTEWEG). If we draw this series of points in the plaitpoint diagram, it must of course satisfy the condition which follows from the fact, that they lie below the three-phase triangle, namely on the side of the small pressures. At low temperatures it lies even in the region of the negative pressures.

Fig. 2 of KUENEN p. 326 must therefore be completed with a theoretic curve which starts at point A , retrogrades immediately to lower temperatures and lies below the curve of the three-phase pressure. The theoretical branch approaches to the same asymptote as the highest branch that starts at C_2 . For the theoretic branch also $\left(\frac{d^2v}{dx^2}\right)$ must be positive, and therefore we have:

$$\frac{dp}{dT} < \left(\frac{\partial p}{\partial T}\right)_v$$

The rapid rising of this branch at low values of T seems to be contradictory to this explanation. But if we take into account that also $\left(\frac{\partial p}{\partial T}\right)_v$ approaches to an infinitely great value for values of v which approach to the limiting volume, this apparent contradiction disappears.

What is surprising, at least to me, is that these theoretic plaitpoints serve to make the course of the practical plaitpoints continuous. But on the other hand the circumstance, that also for the course of these theoretic plaitpoints a so important and at the same time a so simple meaning has been found, confirms my opinion that now the true description of the phenomenon has been given, at least for those cases, in which the longitudinal plait has its summit on the side of the small volumes.

But though the accuracy of the description of the phenomenon has increased, we must acknowledge that the chance to find a satisfactory explanation for the phenomenon is not greater than before; on the contrary it has diminished. The circumstance in which a mixture of two substances has a maximum and a minimum critical temperature needs now no longer be inquired into. The question whether the

size of the molecule of the normal substance has influence on the course, has also lost its direct importance. For mixtures of ethane with an alcohol the separation between the two types lies between methyl- and ethylalcohol; the question whether this separation takes place between two higher terms of the alcohol series, if we take instead of ethane a higher term of the series of carbonhydrogene compounds, which seemed very important before is now no longer of primary interest¹⁾. It seems to me that I have to return in many respects to my original meaning, namely that we have to inquire after the circumstance which causes the spinodal curve to show a protuberance towards the side of the small volumes. In mixtures of a normal substance with an associating one this cause can perhaps be found in the circumstance that the quantity $\left(\frac{\partial p}{\partial x}\right)_v$ can obtain abnormous high values for such a mixture. As the equation:

$$-\frac{\partial p}{\partial v} \frac{\partial^2 \psi}{\partial x^2} = \left(\frac{\partial p}{\partial x}\right)^2$$

applies to the spinodal curve, the value of $-\frac{\partial p}{\partial v}$ may also be abnormally high in this case. If this is really the case an explanation for the protuberance is given which is certainly satisfactory. Yet a great distance exists between this observation and an adequate calculation.

In any case these experiments of KUENEN, to which I hope that he will add many others, are an important contribution to our knowledge of the critical phenomena of not miscible substances.

Physics. — "*The influence of variation of the constant current on the pitch of the singing arc.*" By J. K. A. WERTHEIM SALOMONSON. (Communicated by Prof. P. ZEEMAN).

In the course of some experiments on the physiological action of alternating currents of very high frequency, I tried the currents generated by means of DUBDELL's singing arc. A constant current arc between solid carbons shunted by a self-inductive resistance and a condenser emits a note, the pitch of which corresponds with the frequency of the alternate current generated in the condenser-circuit.

¹⁾ An experiment in order to investigate whether for propane the limit lies between ethyl- and propylalcohol was already in preparation for a long time in the laboratory of Amsterdam. But other labour which could not be delayed prevented each time those who would undertake the investigation.

DUDELL believed that the frequency was determined by the self-induction and the capacity according the well-known formula:
 $p = 2 \pi \sqrt{cL},$

PAUL JANET thought the same and proposed, as DUDELL had already done before, to use the singing arc for measuring small coefficients of self-induction.

In the way proposed by JANET, this seems to be impossible as the frequency depends not only on the self-induction and the capacity but i. a. also on the strength of the constant current.

I have investigated the variation of the frequency caused by varying the constant current, the results being stated in this paper.

The experiments were carried out after PEUKERT's method. The $P D$ at the solid carbons was measured by a Weston-instrument, that showed the Volts of the constant current only, and at the same time by a hot-wire Voltmeter. Lastly the current in the condenser-circuit was measured by means of a hot-wire amperemeter. The three readings being E_1 , E_2 and I_2 , the frequency may be calculated by

$$p = \frac{I_2}{2 \pi c \sqrt{E_2^2 - E_1^2}},$$

c being the capacity of the condenser in farads.

The necessary correction of the instruments was known and has already been applied in the tables. The arc-lamp used was a small shunt-regulator by KÖRTING & MATTHIESEN.

Series 1. Capacity 2,68 mF. Selfinduction: bronze wire spiral of 80 windings; air isolation; diameter 25 centimeter, height 50 centimeter.

The table contains in the

1 st	column:	I_1	the constant current through the arc.
2 nd	"	E_1	the constant current PD of the carbons.
3 rd	"	E_2	the hot-wire voltmeter reading.
4 th	"	E_a	the value of $\sqrt{E_2^2 - E_1^2}$ being the superposed alternating volts.
5 th	"	I_2	the alternating current strength.
6 th	"	p	the number of complete alternations p. s. calculated by PEUKERT's formula.

TABLE I.

I_1	E_1	E_2	E_a	I_2	$p.$
1.9	37.0	44.0	23.7	1.8	4520
2.2	37.0	46.0	27.4	2.4	5230
2.6	37.5	43.0	24.1	2.1	5960
2.8	37.5	44.0	23.0	2.4	6450
3.2	38.0	42.7	19.6	2.5	8000
3.7	38.0	41.0	15.5	2.7	10390
4.1	38.0	40.0	12.8	3.0	13980

Series 2. The same as in Series I. Capacity reduced to 1.68 mF.

TABLE II.

I_1	E_1	E_2	E_a	I_2	$p.$
1.7	38	46	26	1.7	6200
2.4	39	46	24.5	2.1	8130
2.8	39	44	20.4	2.1	9820
3	38	42.7	19.6	2.3	11200
3.5	38.5	42	16.75	2.4	13590
3.7	38	42	18.3	2.7	13980

Series 3. Capacity 1 mF. Selfinduction: coil of 160 windings in 4 layers; wire 2 millimeters. Length of coil 8 centimeters, external diameter 3.5 centimeter.

TABLE III.

I_1	E_1	E_2	E_a	I_2	$p.$
1.9	38	47.7	28.7	2.4	14950
2.3	38	47	26	2.6	17240
2.6	38	45	24.5	2.9	18820
2.9	38	43	20.1	2.8	22200
3.3	37	42	19.8	3.3	26600
3.6	37	42	19.8	3.5	28160
4.1	38	41	15.4	3.4	35100

Series 4. The same as Series III. Capacity reduced to 0.5 mF.

TABLE IV.

I_1	E_1	E_2	E_a	I_2	p .
1.9	35	47	31.3	2.51	25200
2.4	36	42	21.6	2.51	36800
2.7	35	40	19.4	2.7	44300
3.1	35	39	17.2	3	55550
3.4	35	37	12	3.2	84700
3.7	35	36.5	10.36	3.3	97700
3.9	35	36.5	10.36	3.4	100500

Series 5. Capacity 1 mF. Selfinduction: coil of 40 windings in 2 layers; wire $3\frac{1}{2}$ mm. Length of coil 8 centimeter, external diameter 3.5 centimeter.

TABLE V.

I_1	E_1	E_2	E_a	I_2	p .
1.9	38	50.4	33.2	4.68	22400
2.2	38	50.4	33.2	5.16	24700
2.6	38	50.4	33.2	5.55	26700
2.9	38	46	26.0	5.20	31800
3.2	37.6	46	26.5	6.15	37000
3.6	37	44	23.8	6.15	41200
3.7	38	43.2	22.8	6.24	43600
4.2	38	41	15.4	5.70	59200

Series 6. The same conditions as in Series 5. The capacity reduced to 0.3 mF.

TABLE VI.

I_1	E_1	E_2	E_a	I_2	p .
2.1	35	50	35.7	4.1	61300
2.4	36	47.5	31	4.2	71900
2.9	35	42	23.2	4	91600
3.6	36	40.2	17.9	4.4	130000
4.2	35	36.3	9.75	3.6	196000

DUDELL attained frequencies of 500—10000 complete periods p. s. SIMON increased the number of alternations so much, that the note emitted by the arc ceased to be audible. He speaks of a limit of 30000—40000 vibrations. From my tables will be seen that I have attained much higher frequencies, so high that I first distrusted them. But as yet I have not been able to find any inaccuracy either in the principle of the method or in its application. So I must think that my numbers are exact, the more so as they seem to be confirmed by a physiological estimate. With small frequencies, say up to 10000, the pitch of the note may be easily estimated by the ear when we produce two notes in rapid succession. In Series 1 I found that increasing the current from 1.9 to 2.2 ampere caused the pitch to rise about a "second". By increasing from 2.2 ampere to 3.2 ampere the successive notes sounded as with a quint-interval. The later calculation of the frequencies from the galvanometer readings agreed fairly well with the estimated increase of pitch.

The limit of audibility as calculated from the readings agreed equally with the limit as determined by the aid of a recently graduated GALTON-whistle by Prof. EDELMANN, the graduation-table being verified on different points by myself. I found as a limit for the audibility about 43500 d. v. p. s. My arc-lamp ceased to emit an audible note when the frequency of 42000 was reached. In the 6th series no sound was heard at all. In the series 1, 2 and 3 the sound was heard throughout. In the series 4 I heard the note distinctly at 2.4 ampere; at 2.7 ampere I did not always hear the sound; only every now and then I got the impression of a very faint and high whistling sound. At 3.1 ampere I did not hear the sound. In the 5th Series the sound was always present at 3.6 ampere and sometimes at 3.7 ampere.

As these results agree, I think that the method is a correct one, and that the higher numbers may also be relied upon.

The sound of the singing arc may prove perhaps valuable in physiological researches on sound.

The highest frequency with my apparatus was attained with a primary constant current of 4.2 ampere, $E_1 = 36$ Volt, $E_2 = 37.3$ Volt, $I_2 = 0.49$ ampere, $C = 0.03$ m.F., E_a being 9.7 Volt and $p = 268000$. Of course much higher frequencies may probably be attained. But the resistance of my hot-wire amperemeter was rather high, and I believe that therein lies an obstacle for my surpassing this limit.

How are we to interpret the increase of the frequency caused by an increase of the constant current? There is some analogy with

the rise in pitch of electromagnetically driven tuningforks when the intensity of the currents is increased; and also with the rise of the pitch of harmoniumreeds when the air-pressure is increased: Yet there is already some difference in the origin of these last two phenomena, so as to forbid anything more than considering the analogy. The only allowed consequence is, that the electrical system consisting of a capacity and a selfinduction does in this special case not vibrate in its proper period and that this proper period might only be expected to be brought about by a hypothetic infinitely small constant current through the arc.

Increasing the P. D. at the carbons seems to lower the pitch and at the same time to increase the intensity of the sound; if the P.D. rises too much the whistling ceases all at once. As I worked with a constant E. M. F. of 110 Volts from an accumulator-battery, the primary current strength was regulated by inserting resistance or withdrawing it from the circuit. When without changing the resistance, the P. D. at the carbons rises, the current falls off and so causes the frequency to diminish at the same time. Yet by keeping the current constant, by lengthening the arc and withdrawing resistance at the same time an unmistakable lengthening of the period may be observed.

From the Tables I—VI curves have been plotted connecting the frequency with the current-strength.

It is not impossible, that a simple relation might express this connection. Yet an experimental formula as

$$p = a + b I + c I^2$$

is only possible when b is negative; as in this case there is a minimum for $I = \frac{b}{2c}$ this formula does not seem to be very plausible.

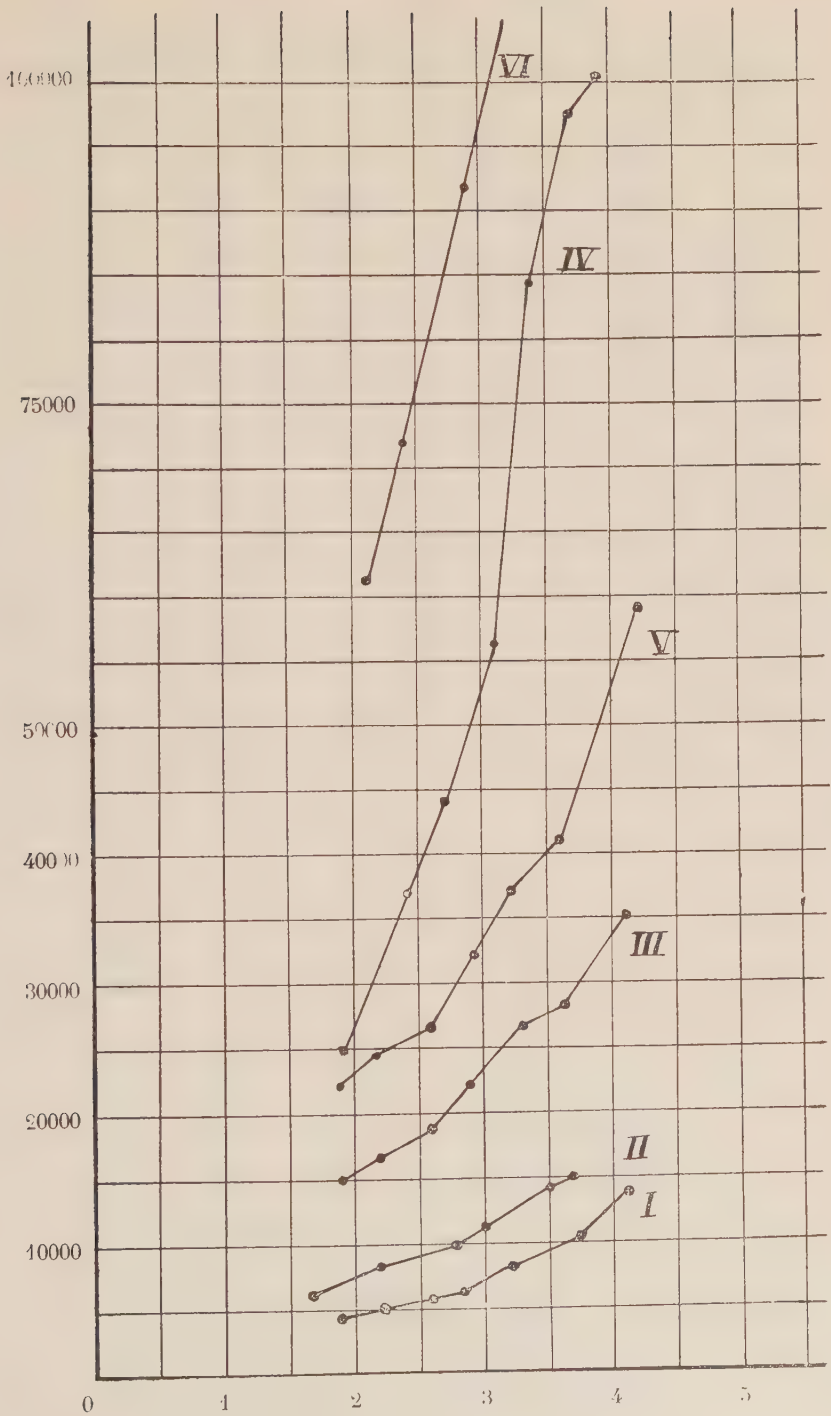
I have also tried a quadratic expression connecting the steadying resistance with the frequency, but this did not give satisfaction.

At last I found as the most simple formula and agreeing best with the observed results:

$$\log p = a + b I,$$

in which a and b are constants, p the frequency and I the constant current intensity.

I found for series 1:



$$\log p = 3.23522 + 0.2165 I.$$

<i>I</i>	<i>log p</i> (calc.)	<i>log p</i> (obs.)	ρ	<i>p</i> (calc.)	<i>p</i> (obs.)
1.9	3.64757	3.65514	+ 0.00857	4432	4520
2.2	3.74152	3.71850	+ 0.00698	5147	5230
2.6	3.79812	3.77525	— 0.02287	6282	5960
2.8	3.84142	3.80956	— 0.03186	6941	6450
3.2	3.92802	3.90309	— 0.02493	8473	8000
3.7	4.03627	4.01662	— 0.01965	10871	10390
4.1	4.12287	4.14364	+ 0.02077	13270	13920

The mean error of *log p* being: $\sqrt{\frac{1}{6} \Sigma (\rho)^2} = 0.02272$ the error-factor of *p* is 1.053 and the mean error of *p* is 5.3 %.

Considering that 3 galvanometer readings are necessary which individually ought to have errors of much less than 0.5 %, but which are to be taken all at the same time and therefore are more inaccurate, a mean error of 5.3 % in the result, representing an interval of less than a tone may not be called extravagant.

For series 2. I find: $\log p = 3.47786 + 0.18453 I.$

<i>I</i>	<i>log p</i> (calc.)	<i>log p</i> (obs.)	ρ	<i>p</i> (calc.)	<i>p</i> (obs.)
1.7	3.79156	3.79239	+ 0.00083	6189	6200
2.4	3.92073	3.91009	— 0.01064	8332	8130
2.8	3.99454	3.99211	— 0.00243	9875	9820
3.0	4.03145	4.04922	+ 0.01777	10751	11200
3.5	4.12371	4.13322	+ 0.00951	13296	13590
3.7	4.16062	4.14551	— 0.01511	14475	13980

$$\rho_m = \sqrt{\frac{1}{5} \Sigma (\rho)^2} = 0.01228$$

the mean error of one observation being 2.867 %.

Series 3. $\log p = 3.84563 + 0.17062 I.$

I	$\log p$ (calc.)	$\log p$ (obs.)	ρ	p (calc.)	p (obs.)
1.9	4.46981	4.47464	0.00483	44785	44950
2.3	4.23806	4.23654	0.00152	47300	47240
2.6	4.28927	4.27462	0.01465	49466	48820
2.9	4.34043	4.34635	0.00592	21900	22200
3.3	4.40868	4.42488	0.01620	25626	26600
3.6	4.45986	4.44963	0.01023	28831	28160
4.1	4.54517	4.54531	0.00014	35089	35160

$$\sigma m = \sqrt{\frac{1}{6} \Sigma (\rho)^2} = 0.01035$$

mean error of one observation 2.412 %.

Series 4. $\log p = 3.80102 + 0.31641 I.$

I	$\log p$ (calc.)	$\log p$ (obs.)	ρ	p (calc.)	p (obs.)
1.9	4.40220	4.40140	— 0.00080	25247	25200
2.4	4.56280	4.56585	+ 0.00305	36542	36800
2.7	4.65532	4.64640	— 0.00892	45219	44300
3.1	4.78189	4.74468	— 0.03721	69519	55550
3.4	4.87681	4.92788	+ 0.05107	75303	84700
3.7	4.97174	4.98989	+ 0.01815	93700	97700
3.9	5.03502	5.00217	— 0.03285	108400	100500

$$\sigma m = \sqrt{\frac{1}{6} \Sigma (\rho)^2} = 0.02994$$

mean error of one observation 7.14 %.

Series 5. $\log p = 3.98960 + 0.17902 I.$

I	$\log p$ (calc.)	$\log p$ (obs.)	ρ	p (calc.)	p (obs.)
1.9	4.32974	4.35025	+ 0.02051	21367	22400
2.2	4.38344	4.39270	+ 0.00926	24179	24700
2.6	4.45505	4.42651	- 0.02854	28513	26700
2.9	4.50876	4.50243	- 0.00633	32267	31800
3.2	4.56246	4.56820	+ 0.00574	36514	37000
3.6	4.63407	4.61490	- 0.01917	43060	41200
3.7	4.65197	4.63949	- 0.01248	44871	43600
4.2	4.74148	4.77232	+ 0.03084	55141	59200

$$\varrho m = \sqrt{\frac{1}{7} \sum (\varrho)^2} = 0.02024$$

mean error of one observation 4.77 %.

Series 6. $\log p = 4.31949 + 0.22466 I.$

I	$\log p$ (calc.)	$\log p$ (obs.)	ρ	p (calc.)	p (obs.)
2.1	4.79128	4.78746	- 0.00382	61841	61300
2.4	4.85867	4.85673	- 0.00194	72222	71900
2.9	4.97100	4.96190	- 0.00910	93540	91600
3.6	5.12827	5.11394	- 0.01433	134360	130000
4.2	5.26306	5.29226	+ 0.02920	183257	196000

$$\varrho m = \sqrt{\frac{1}{4} \sum (\varrho)^2} = 0.01702$$

mean error of one observation 4.00 %.

The empirical formula represents fairly well the observed results in the range of the experiment. But it does not give more than that, I do not think that it may be used for extrapolating. This will be directly seen, when we extrapolate for the intensity = 0. We calculate for the frequency at the intensity = 0 in the 4th series: 6324 d. v. and in the 3rd series: 7009 d. v. Theoretically the frequency in series 4 should be exactly $\sqrt{2}$ times higher than in series 3.

A more exact method may perhaps give numbers from which a better formula might be deduced, and which at the same time might give us some insight in the phenomenon.

I have tried to get more exact numbers by means of the KUNDT dust-figures but I did not succeed, though others might. Yet the oscillatory discharge of a Leyden jar through an inductive resistance easily gave regular dust-figures. The reason why the KUNDT-method proved refractory with the singing arc, is not easy to be understood: I can only suppose that the intensity of the sound is not large enough.

Physics. — Dr. J. E. VERSCHAFFELT. "*Contributions to the knowledge of VAN DER WAALS' ψ -surface. VII. The equation of state and the ψ -surface in the immediate neighbourhood of the critical state for binary mixtures with a small proportion of one of the components*". Communication n°. 81 from the Physical Laboratory at Leiden, by Prof. H. KAMERLINGH ONNES. ¹⁾

(Communicated in the meeting of June 28, 1902).

Introduction.

In Communication n°. 65 from the Physical Laboratory at Leiden ²⁾ I have given the first results of a treatment of my measurements on mixtures of carbon dioxide and hydrogen ³⁾ by the method which KAMERLINGH ONNES ⁴⁾ alone and with REINGANUM ⁵⁾ used for the measurements of KUENEN on mixtures of carbon dioxide and methyl chloride ⁶⁾. They confirm KAMERLINGH ONNES' opinion that the isothermals of mixtures of normal substances may be derived, by means of the law of corresponding states, from the general empirical reduced equation of state for which he has given in communications nrs. 71 ⁷⁾ and 74 ⁸⁾ a development in series indicated in communication 59a. In this empirical reduced equation of state

$$p = \frac{a}{\lambda v} + \frac{b}{\lambda^2 v^2} + \dots,$$

¹⁾ The translation of the first and second part of this article are treated as a whole, hence some minor changes in text will be found.

²⁾ Arch. Néerl., (2), 5, 644, 1900; Comm. phys. lab. Leiden, n°. 65.

³⁾ Thesis for the doctorate, Leiden, 1899.

⁴⁾ Proc. Royal Acad., 29 Sept. 1900, p. 275; Comm. 59a.

⁵⁾ Ibid. p. 289; Comm., n°. 59b.

⁶⁾ Thesis for the doctorate, Leiden, 1892.

⁷⁾ Proc. Royal Acad., June 1901; Comm., n°. 71.

⁸⁾ Arch. Néerl., (2), 6, 874, 1901; Comm., n°. 74.

where \mathfrak{U} , \mathfrak{V} etc. represent series of the powers of the reduced absolute temperature t , with co-efficients which like λ are the same for all substances, we then put:

$$t = \frac{T}{T_{xk}}, \quad \mathfrak{p} = \frac{p}{p_{xk}}, \quad \mathfrak{v} = \frac{v}{v_{xk}},$$

T_{xk} , p_{xk} and v_{xk} standing for the critical elements of the mixture with molecular composition x , if it remained homogeneous, while

$$\lambda = \frac{p_{xk} v_{xk}}{T_{xk}}.$$

It must therefore also be possible to find expressions for the critical quantities of a mixture — these are the elements p_{xpl} , v_{xpl} , T_{xpl} of the plaitpoint and p_{xr} , v_{xr} , T_{xr} of the critical point of contact — in which only the co-efficients of the general empirical reduced equation of state and further the quantities characteristic of the mixture viz. T_{xk} , p_{xk} , v_{xk} , occur, or the co-efficients of the developments in series of these quantities in powers of x . In the case of mixtures with small values of x , it may, exclusive of exceptional cases, suffice, to a first approximation, to introduce the co-efficients:

$$\alpha = \frac{1}{T_k} \frac{dT_{xk}}{dx} \text{ and } \beta = \frac{1}{p_k} \frac{dp_{xk}}{dx}.$$

A first step towards realizing this idea of KAMERLINGH ONNES has been made by KEESOM¹⁾ who took for his basis the general equations by which VAN DER WAALS in his *Théorie moléculaire* and following papers has expressed the relation of the critical quantities and the composition; he has found what these equations would become for infinitely small x -values and has introduced into them the co-efficients α and β mentioned above, besides others which might be derived from the co-efficients of the general empirical equation of state. I have now tried to work out this idea in a method which is more closely connected to the treatment of the ψ -surface, namely by developing the co-efficients of the equation of state and the equation of the ψ -surface in the powers of x . On account of the great complication involved by the introduction of the higher co-efficients into the calculation, I have confined myself to the lower powers of x . However, the method followed by me can also be used to find the co-efficients of higher powers.

As I have confined myself to states in the neighbourhood of the critical point I could use instead of KAMERLINGH ONNES' empirical reduced equation of state the more simple one which it becomes within narrow limits of temperature and volume on developing the different

¹⁾ Proc. Royal. Acad., 28 Dec. 1901, p. 293; Comm., n^o. 75.

terms in powers of the small quantities $v-1$ and $t-1$. According to VAN DER WAALS' method ¹⁾ I wrote this new equation:

$$p = 1 + \frac{\partial p}{\partial t} (t-1) + \dots + \frac{\partial^2 p}{\partial v \partial t} (v-1) (t-1) + \dots \quad (1)$$

where the co-efficients $\frac{\partial p}{\partial t}$, $\frac{\partial^2 p}{\partial v \partial t}$ etc. can be immediately derived from those of the above mentioned empirical reduced equation of state.

1. *The p, v, T diagram for a simple substance in the neighbourhood of the critical point.*

In order to limit the number of the continually re-occurring factors as much as possible, I shall not write the equation of state of the pure substance in a reduced form, but thus:

$$p = k_0 + k_1 (v-v_k) + k_2 (v-v_k)^2 + k_3 (v-v_k)^3 + \dots = f(v). \quad (2)$$

where k_0 , k_1 , k_2 etc. are temperature functions which can be developed in powers of $T-T_k$; as for instance:

$$k_0 = k_{00} + k_{01} (T-T_k) + k_{02} (T-T_k)^2 + \dots \quad (2')$$

and it is evident that $k_{00} = p_k$ while k_{10} and k_{20} are zero.

We might clearly find the equations of several curves in this diagram, such as: the border curve, the curve of the maximum or minimum pressures, the curve of the points of inflection etc. I shall derive the former only, chiefly in order to apply to a simple case the method of calculation to be used afterwards for finding the pressure, volume and composition of the co-existing phases with mixtures.

If v_2 and v_1 represent the molecular volumes of the vapour and of the liquid, co-existing at the temperature T under the pressure p_1 , then these 3 unknown quantities will be determined by the equations:

$$p_1 = f(v_1), \quad p_1 = f(v_2) \quad \dots \quad (3)$$

and by MAXWELL's criterium

$$p_1 (v_2 - v_1) = \int_{v_1}^{v_2} p \, dv \quad \dots \quad (4)$$

The two unknown quantities v_2 and v_1 I shall, however, replace by the two infinitely small quantities $\frac{1}{2}(v_2 + v_1) - v_k = \Phi$ and $\frac{1}{2}(v_2 - v_1) = \varphi$; Φ is therefore the abscissa of the diameter of the border curve for chords parallel with the v -axis, and φ is the half chord.

¹⁾ Zeitschr. f. physik. Chem., 13, 694, 1894.

Equation (4) after division by 2 φ yields:

$$p_1 = k_0 + k_1 \Phi + k_2 (\Phi^2 + \frac{1}{3} \varphi^2) + k_3 \Phi (\Phi^2 + \varphi^2) + k_4 (\Phi^4 + 2 \Phi^2 \varphi^2 + \frac{1}{5} \varphi^4) + \dots (5)$$

where for completeness I have not regarded the order of the different terms. Also taking equation (3) once for v_1 and once for v_2 and adding together, yields:

$$p_1 = k_0 + k_1 \Phi + k_2 (\Phi^2 + \varphi^2) + k_3 \Phi (\Phi^2 + 3 \varphi^2) + k_4 (\Phi^4 + 6 \Phi^2 \varphi^2 + \varphi^4) + \dots (6)$$

and subtracting and dividing by 2 φ gives

$$0 = k_1 + 2k_2 \Phi + k_3 (3 \Phi^2 + \varphi^2) + 4k_4 \Phi (\Phi^2 + \varphi^2) + \dots (7)$$

while the, at least to a first approximation simpler equation:

$$0 = \frac{2}{3} k_2 + 2k_3 \Phi + 4k_4 \left(\Phi^2 + \frac{1}{5} \varphi^2 \right) + \dots (8)$$

follows from (5) and (6).

The equations (6), (7) and (8) now determine the quantities Φ , φ and $p_1 - p_k$; for we find:

$$\varphi^2 = - \frac{k_{11}}{k_{30}} (T - T_k) - \dots (9)$$

$$\Phi = - \frac{1}{k_{30}} \left(\frac{1}{3} k_{21} - \frac{2}{5} \frac{k_{11} k_{40}}{k_{30}} \right) (T - T_k) - \dots (10)$$

$$p_1 - p_k = k_{01} (T - T_k) + \dots (11)$$

Along the border curve $v = v_k + \Phi \pm \varphi$, so that we may write the equation of the border curve:

$$0 = (v - v_k)^2 - 2(v - v_k) \Phi + \Phi^2 - \varphi^2, \dots (12)$$

and to the first approximation this represents a parabola²⁾.

1) Just as v. D. WAALS (Arch. Néerl. (1), 28, 171) from the reduced equation of state $p = \frac{8t}{3v-1} - \frac{3e^{1-t}}{v^3}$ has derived $\frac{1}{2}(v_2 - v_1) = 2\sqrt{2(1-t)}$, I have also derived $\frac{1}{2}(v_2 + v_1)$ from the same equation by means of the reduced formula (10) and have found for it:

$$\frac{1}{2}(v_2 + v_1) = 1 + 7,2(1-t),$$

whence, if ρ_1 and ρ_2 stand for the liquid and vapour densities:

$$\frac{1}{2}(\rho_2 + \rho_1) = \rho_k [1 + 0,8(1-t)]$$

From AMAGAT's data for carbon dioxide I find:

$$\Delta = \frac{1}{2}(\rho_2 + \rho_1) = 0,464 + 0,001181(T_k - T),$$

or reduced $1 + 0,775(1-t)$, and for isopentane (S. YOUNG's data)

$$\Delta = \rho_k [1 + 0,881(1-t)].$$

The above equation of state, therefore, represents the diameter numerically in a satisfactory manner.

2) The same problem with regard to φ has been treated by v. D. WAALS (loc. cit.) in a somewhat different way; only φ is determined accurately by his method and the border curve can be derived from his formulae only to a first approximation.

2. The p , v , T diagram of a mixture with a small value of x near the critical point of the homogeneous mixture.

From the consideration we have started from it follows immediately that we obtain the system of isothermals of the mixture by moving that of the pure substance to an infinitely small amount parallel to itself so that the critical point (p_k, v_k) is brought on to the critical point of the homogeneous mixture (p_{xk}, v_{xk}) , and at the same time by expanding it infinitely little parallel to its co-ordinates in multiplying the ordinates by $\frac{p_{xk}}{p_k}$ and the abscissae by $\frac{v_{xk}}{v_k}$. Moreover an isothermal, belonging to the temperature T in the first system will belong to the temperature $\frac{T_{xk}}{T_k}T$ after we have moved and magnified the system.

We put again:

$$p = l_0 + l_1(v - v_{xk}) + l_2(v - v_{xk})^2 + l_3(v - v_{xk})^3 + \dots \quad (13)$$

where l_0, l_1, l_2 etc. are once more functions of the temperature, thus:

$$l_0 = l_{00} + l_{01}(T - T_{xk}) + l_{02}(T - T_{xk})^2 + \dots \quad (13')$$

According to the derivation from the reduced equation of state by means of T_{xk} , p_{xk} , v_{xk} the co-efficients l_{00} , l_{01} , ..., l_{10} , l_{11} etc. are only functions of x . Putting:

$$T_{xk} = T_k(1 + \alpha x + \alpha'x^2 + \dots)$$

$$p_{xk} = p_k(1 + \beta x + \beta'x^2 + \dots) \quad \dots \quad (14)$$

$$v_{xk} = v_k(1 + \gamma x + \gamma'x^2 + \dots)$$

where

$$\gamma = \alpha - \beta, \quad \gamma' = \alpha' - \beta' - \alpha\beta + \beta^2 \text{ etc.}, \quad \dots \quad (14')$$

we find

$$\begin{aligned} l_{00} &= p_k[1 + \beta x + \dots], \quad l_{01} = k_{01}[1 - (\alpha - \beta)x + \dots], \quad l_{02} = k_{02}[1 - (2\alpha - \beta)x + \dots], \dots \\ l_{10} &= 0, \quad l_{11} = k_{11}[1 - 2(\alpha - \beta)x + \dots], \quad l_{12} = k_{12}[1 - (3\alpha - 2\beta)x + \dots], \dots \\ l_{20} &= 0, \quad l_{21} = k_{21}[1 - 3(\alpha - \beta)x + \dots], \dots \\ l_{30} &= k_{30}[1 - (3\alpha - 4\beta)x + \dots], \dots \\ l_{40} &= k_{40}[1 - (4\alpha - 5\beta)x + \dots], \dots; \quad \dots \quad (15) \end{aligned}$$

where all co-efficients l are expressed in co-efficients k as well as in KAMERLINGH ONNES' α 's and β 's.

From the values of T_{xk} , p_{xk} , v_{xk} , with mixtures of carbon dioxide with small quantities of hydrogen for $x = 0$, $x = 0,05$ and $x = 0,1$,¹⁾ I find:

¹⁾ Comm., n^o. 65.

$$\begin{aligned}
T_{xk} &= T_k (1 - 1,17 x + 1,58 x^2) \\
p_{xk} &= p_k (1 - 1,62 x + 2,45 x^2) \quad . \quad . \quad . \quad . \quad (16) \\
v_{xk} &= v_k (1 + 0,62 x - 0,95 x^2), ^1)
\end{aligned}$$

while from (14) would follow:

$$v_{xk} = v_k (1 + 0,45 x + 0,08 x^2).$$

Although the agreement between the two expressions for v_{xk} is not quite satisfactory, it yet by no means indicates that the law of corresponding states does not hold; it may very well be a result of the uncertainty of the critical data of the homogeneous mixtures, chiefly of the v_{xk} 's. Besides from the second formula for v_{xk} I find:

for $x = 0,05$ $v_{xk} = 0,00432$ and for $x = 0,1$ $v_{xk} = 0,00441$, and these values deviate from those determined directly (0,00434 and 0,00444) not more than the amount of the error that can be made in these determinations. Besides, since the law of corresponding states does not hold entirely with pure substances, it is not likely to do so for mixtures.

3. The p, v, x diagram for mixtures with a small value of x , at a temperature differing little from T_k .

We shall now consider different mixtures at the same temperature T ; the system of isothermals in the p, v, x diagram, at that temperature is represented by the equation of state (13), where, however, T must now be taken as constant and x as variable. We will now put this equation in another and more suitable form.

Among all the mixtures there is one for which the critical temperature would be T if this mixture remained homogeneous; the composition x_{Tk} of this mixture, and also the critical elements p_{Tk} and v_{Tk} are determined by equation (14). (In this equation we must put: $T_{xk} = T$, $x = x_{Tk}$, $p_{xk} = p_{Tk}$ and $v_{xk} = v_{Tk}$).

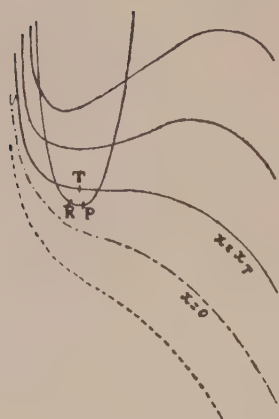
Hence we find to a first approximation

$$x_{Tk} = \frac{T - T_k}{\alpha T_k}, \quad p_{Tk} = p_k + \frac{p_k \beta}{\alpha T_k} (T - T_k), \quad v_{Tk} = v_k + \frac{v_k (\alpha - \beta)}{\alpha T_k} (T - T_k). \quad (17)$$

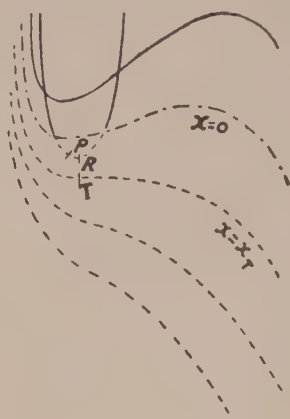
It will be seen that to a first approximation the value x_{Tk} is either positive or negative according as $T - T_k$ and α have the same or opposite signs, that is to say

	$\alpha > 0$	$\alpha < 0$
$T > T_k$	$x_{Tk} > 0$; figs. 1 and 7	$x_{Tk} < 0$; figs. 3, 5, 9 and 11
$T < T_k$	$x_{Tk} < 0$; figs. 2 and 8	$x_{Tk} > 0$; figs. 4, 6, 10 and 12

²⁾ Comp. also KEESOM, *loc. cit.*, p. 12.



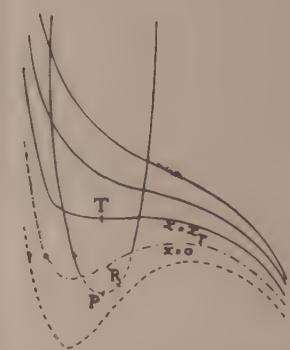
$m_{01} > 0$, $\alpha > 0$, $RT_k^2 k_{11} \alpha < m_{01}^2$, $T > T_k$.
Fig. 1.



$m_{01} > 0$, $\alpha > 0$, $RT_k^2 k_{11} \alpha < m_{01}^2$, $T < T_k$.
Fig. 2.



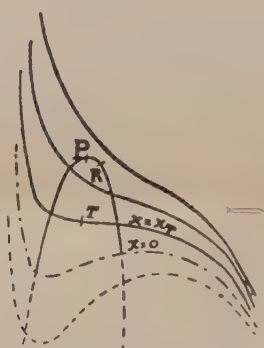
$m_{01} > 0$, $\alpha < 0$, $RT_k^2 k_{11} \alpha < m_{01}^2$, $T > T_k$.
Fig. 3.



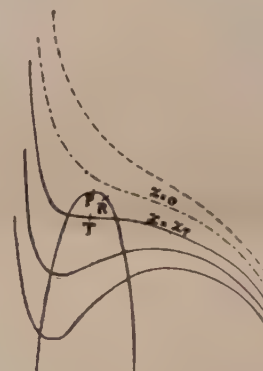
$m_{01} > 0$, $\alpha < 0$, $RT_k^2 k_{11} \alpha < m_{01}^2$, $T < T_k$.
Fig. 4.



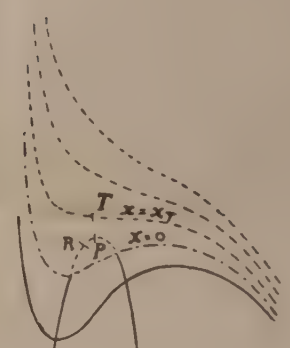
$m_{01} > 0$, $\alpha < 0$, $RT_k^2 k_{11} \alpha > m_{01}^2$, $T > T_k$.
Fig. 5.



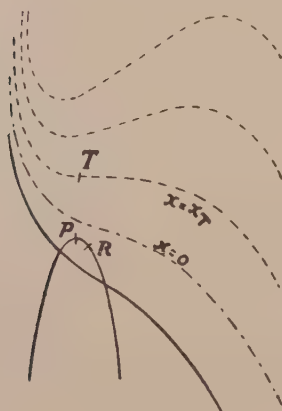
$m_{01} > 0$, $\alpha < 0$, $RT_k^2 k_{11} \alpha > m_{01}^2$, $T < T_k$.
Fig. 6.



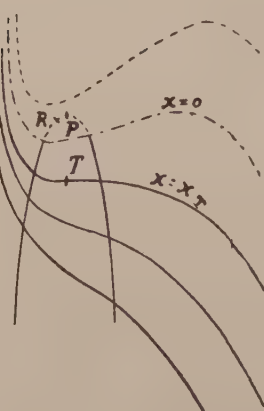
$m_{01} < 0$, $\alpha > 0$, $RT_k^2 k_{11} \alpha < m_{01}^2$, $T > T_k$.
Fig. 7.



$m_{01} < 0$, $\alpha > 0$, $RT_k^2 k_{11} \alpha < m_{01}^2$, $T < T_k$.
Fig. 8.



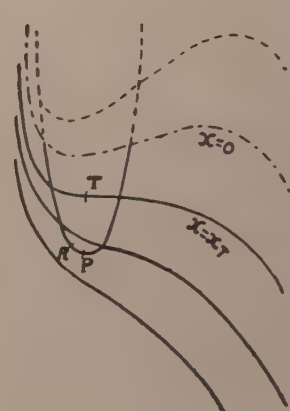
$m_{01} < 0$, $\alpha < 0$, $RT_k^2 k_{11} \alpha < m_{01}^2$, $T > T_k$.
Fig. 9.



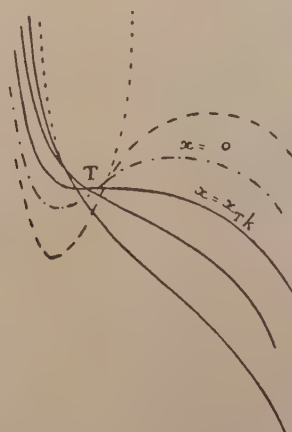
$m_{01} < 0$, $\alpha < 0$, $RT_k^2 k_{11} \alpha < m_{01}^2$, $T < T_k$.
Fig. 10.



$m_{01} < 0$, $\alpha < 0$, $RT_k^2 k_{11} \alpha > m_{01}^2$, $T > T_k$.
Fig. 11.



$m_{01} < 0$, $\alpha < 0$, $RT_k^2 k_{11} \alpha > m_{01}^2$, $T < T_k$.
Fig. 12.



$m_{01} = 0$, $\alpha < 0$, $T < T_k$, $m_{02} < 0$.
Fig. 13.

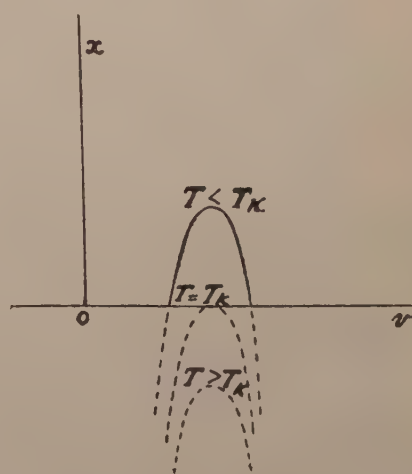


Fig. 14.

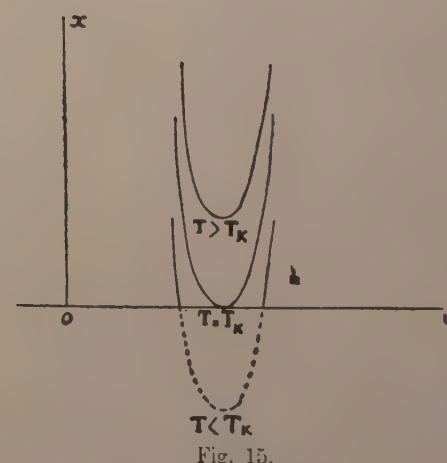


Fig. 15.

Although from a physical point of view x can only take positive values, in these considerations even the case $x_{Tk} < 0$ is not impossible; for the point p_{Tk} , v_{Tk} has only a mathematical meaning.

In general, equation (13) may now be written thus:

$$p = m_0 + m_1(v - v_{Tk}) + m_2(v - v_{Tk})^2 + m_3(v - v_{Tk})^3 + \dots, \quad (18)$$

where m_0 , m_1 etc. are functions of x which can be developed in powers of $x - x_{Tk}$; for instance:

$$m_0 = m_{00} + m_{01}(x - x_{Tk}) + m_{02}(x - x_{Tk})^2 + \dots \quad (18')$$

The co-efficients m are functions of the temperature which is here considered constant; it will be obvious that $m_{00} = p_{Tk}$, while m_{10} and $m_{20} = 0$. By equalization of (18) with (13) we can express all the m 's in the k 's, and in KAMERLINGH ONNES' α 's and β 's; for we find:

$$m_{n0} = k_{n0} - \frac{k_{n0}}{T_k \alpha} [n\alpha - (n+1)\beta] (T - T_k) + \dots$$

$$m_{n1} = -k_{n0}[n\alpha - (n+1)\beta] - k_{n1}T_k\alpha - (n+1)k_{(n+1)0}(\alpha - \beta)v_k + \dots, \text{ etc.} \quad (19)$$

so that to a first approximation:

$$m_{80} = k_{80}, \quad m_{40} = k_{40}, \dots$$

$$m_{01} = pk\beta - k_{01}T_k\alpha, \quad m_{11} = -k_{11}T_k\alpha, \quad m_{21} = -k_{21}T_k\alpha - 3k_{30}v_k(\alpha - \beta), \text{ etc.} \quad (19')$$

HARTMAN¹⁾ has given a diagrammatical representation of the p, v, x diagram. This representation completely resembles a p, v, T diagram; but this resemblance is not necessary. It follows directly from the p, v, T diagram that k_{01} is positive, while k_{11} and k_{30} are negative; in the p, v, x diagram m_{30} is negative, but according to (19), m_{01} and m_{11} may be either positive or negative. The circumstance $m_{01} < 0$ does not indeed influence the general shape of the diagram; it indicates that the isothermals of the mixtures lie below those of the pure substance as is the case at the upper limit ($x = 1$) of HARTMAN's representation²⁾. But while in the p, v, T diagram the isothermals with maximum and minimum pressure occur under the critical, the opposite may be the case in the p, v, x diagram, if m_{01} and m_{11} have the same sign. The four cases which may now present themselves, leaving out very particular values of the coefficients, are given in the following table:

¹⁾ Thesis for the doctorate, Leiden 1899, p. 6; Journ. of Phys. Chem., 5, 425, 1901.

²⁾ From a mathematical point of view we may imagine the p, v, x diagram to be continued outside the limits $x = 0$ and $x = 1$. It is also obvious that x , if differing little from 1, means the same as x infinitely small and that $x > 1$ means the same as $x < 0$.

	$m_{01} > 0$ or $\frac{\beta}{\alpha} > \frac{T_k}{p_k} k_{01}$	$m_{01} < 0$ or $\frac{\beta}{\alpha} < \frac{T_k}{p_k} k_{01}$
$m_{11} > 0$ or $\alpha > 0$	figs. 1 and 2 ¹⁾	figs. 7 and 8
$m_{11} < 0$ or $\alpha < 0$	figs. 3, 4, 5 and 6	figs. 9, 10, 11 and 12.

HARTMAN's diagram represents at the lower limit the case $m_{01} > 0$ and $m_{11} < 0$, at the superior $m_{01} < 0$ and $m_{11} > 0$. The case $\alpha > 0$ will in general occur when the second is less volatile than the first substance; this for instance is the case when methyl chloride is added to carbon dioxide²⁾. On the other hand we shall find the case $\alpha < 0$ when the second substance is the more volatile, when for instance hydrogen is added to carbon dioxide (comp. formulae 16) or carbon dioxide to methyl chloride³⁾.

A p, v, x diagram based on observations has, so far as I know, not yet been published. A diagram of this kind which I have drawn from my measurements on mixtures of carbon dioxide and hydrogen perfectly resembles the p, v, T diagram after HARTMAN, so that in the neighbourhood of pure carbon dioxide we must have $m_{01} > 0$ and $m_{11} < 0$; according to formula (16) α is really negative, while with $k_{01} = 1,61$ (comp. KEESOM *loc. cit.*, p. 14) I find $m_{01} = 454$, and positive. For carbon dioxide with a small quantity of methyl chloride⁴⁾ $\alpha = 0,378$ and $\beta = 0,088$, and hence $m_{01} < 0$ and $m_{11} > 0$; and for methyl chloride with a small quantity of carbon dioxide, $\alpha = -0,221$ and $\beta = 0,281$ so that $m_{01} > 0$ and $m_{11} < 0$. At temperatures between the critical temperatures of the two pure substances, the p, v, x diagram for mixtures of carbon dioxide and methyl chloride will probably correspond to HARTMAN's drawing.

While two neighbouring isothermals ($T, T + dT$) never intersect in the p, v, T diagram (the $\left(\frac{\partial p}{\partial T}\right)_v$ never being zero) this may be the case in the p, v, x diagram for two neighbouring mixtures

¹⁾ Figs. 1—13 represent diagrammatically p, v, x curves for infinitely small values of x and $T - T_k$, such as they appear in reality for finite values of x and $T - T_k$. They are moreover theoretically extended into the imaginary region $x < 0$. All lines lying within the region of negative x are dotted; the isothermal $x = 0$ is represented by a dot-dash line. The line $x = x_{T_k}$ (erroneously marked x_T in figs. 1—12) would be the critical isotherm of the homogeneous mixture.

²⁾ Comp. KAMERLINGH ONNES and REINGANUM, *loc. cit.*, p. 35.

³⁾ *Ibidem.*

⁴⁾ Comp. KEESOM, Comm. n^o. 79, p. 8.

Instead of the third condition I find it however better to use another which follows from all three, viz.

$$M_2 = M_1 \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot (21')$$

where

$$M = \psi - (v - v_{Tk}) \frac{\partial \psi}{\partial v} - (x - x_{Tk}) \frac{\partial \psi}{\partial x}.$$

Corresponding to a former transformation now I write

$$\frac{1}{2}(v_2 + v_1) - v_{Tk} = \Phi \quad \text{and} \quad \frac{1}{2}(v_2 - v_1) = \varphi$$

and equally

$$\frac{1}{2} (x_2 + x_1) - x_{Tk} = \Xi \quad \text{and} \quad \frac{1}{2} (x_2 - x_1) = \mathfrak{S},$$

and I consider the infinitely small quantities Φ , φ , Ξ and ξ as functions of the same variable, viz. $p_1 \dots p_{T_k}$. Thus I find to the first approximation ¹⁾

$$\Phi = -\frac{1}{2m_{s_0}} \left[\frac{1}{3} \frac{m_{s_0}^3}{R^2 T^3} + \frac{m_{s_0} m_{s_1}}{RT} + \frac{2}{3} m_{s_1} - \frac{4}{5} \frac{m_{s_0} m_{s_4}}{m_{s_0}} \left(\frac{m_{s_0}^3}{RT} + m_{s_1} \right) \right] \frac{p_1 - p_{Tk}}{m_{s_0}} - \frac{m_{s_0}}{2RTm_{s_0}} \left[\frac{1}{3} \frac{m_{s_0}^2}{RT} + m_{s_1} - \frac{4}{5} \frac{m_{s_0} m_{s_4}}{m_{s_0}} \right] x_{Tk} \quad (22)$$

$$\varphi^2 = -\frac{1}{m_{30}} \left[\frac{m_{01}^2}{RT} + m_{11} \right] \frac{p_1 - p_{Tk}}{m_{01}} - \frac{m_{01}^2}{RT m_{30}} x_{Tk}, \quad (23)$$

[illegible]

and

$$\xi = \frac{m_{01}}{RT} \varphi \left[\frac{p_1 - p T k}{m_{01}} + x T k \right]; \quad . \quad . \quad . \quad . \quad (25)$$

where x_{T_k} and p_{T_k} may be replaced by their expression (17).

6. *The plaitpoint.*

In the plaitpoint the co-existing phases become identical. If we represent the elements of the plaitpoint by x_{Tpl} , p_{Tpl} and v_{Tpl} then

¹⁾ The four equations from which I derive the relations (22)—(25) are:

$$\left(\frac{\partial \psi}{\partial x}\right)_2 = \left(\frac{\partial \psi}{\partial x}\right)_1, M_2 = M_1, \left(\frac{\partial \psi}{\partial v}\right)_2 = \left(\frac{\partial \psi}{\partial v}\right)_1 \text{ and } p_1 \doteq -\frac{1}{2} \left[\left(\frac{\partial \psi}{\partial v}\right)_2 + \left(\frac{\partial \psi}{\partial v}\right)_1 \right]$$

The two first equations contain the expression $\log \frac{x_2}{x_1}$; as all the other terms are

infinitely small, this must also be the case with $\log \frac{x_2}{x_1}$, in other words, the ratio $\frac{x_2}{x_1}$ can differ only infinitely little from 1; ξ must therefore be of a higher order than $\frac{1}{H}$.

so that also $\log \frac{x_2}{x_1}$ may be developed in a series in powers of $\frac{s}{H+x_{Tk}}$.

at that point $\phi = v_{T_{pl}} - v_{T_k}$, $\varphi = 0$, $\Xi = x_{T_{pl}} - x_{T_k}$ and $\xi = 0$, while $p_1 = p_{T_{pl}}$; thus we obtain, from the equations (22), (23) and (24),

$$x_{T_{pl}} = \frac{RTm_{11}}{m_{01}^2 + RTm_{11}} x_{T_k}, \dots \dots \dots (26)$$

$$p_{T_{pl}} = p_{T_k} - \frac{m_{01}^3}{m_{01}^2 + RTm_{11}} x_{T_k}, \dots \dots \dots (27)$$

and

$$v_{T_{pl}} = v_{T_k} + \frac{m_{01}}{2m_{30}(m_{01}^2 + RTm_{11})} \left[\frac{2}{3} m_{01}m_{21} - \frac{1}{3} \frac{m_{01}^2 m_{11}}{RT} - m_{11}^2 \right] x_{T_k} \dots (28)$$

If x_{T_k} , p_{T_k} , and v_{T_k} are replaced by their expressions (17), the elements of the plaitpoint are thereby determined to the first approximation as functions of the temperature T ; RTm_{11} may then be replaced by $RT_k m_{11}$.

From equations (26) and (27) follows immediately :

$$\frac{p_{T_{pl}} - p_{T_k}}{x_{T_{pl}} - x_{T_k}} = m_{01} \dots \dots \dots (29)$$

In order to see how this relation holds for mixtures of carbon dioxide and hydrogen I consider the temperature $27,10^\circ \text{C.}$ at which the mixture $x = 0,05$ has its plaitpoint ($p_{T_{pl}} = 91,85 \text{ atm.}$); at that temperature $x_{T_k} = 0,011$ and $p_{T_k} = 72,4 \text{ atm.}$ so that $\frac{p_{T_{pl}} - p_{T_k}}{x_{T_{pl}} - x_{T_k}} = 500$, in good agreement with the value 454 which I have found for m_{01} .

It follows from equation (26) that $x_{T_{pl}}$ can be positive or negative. As $x_{T_k} < 0$ is not impossible, this is equally the case with $x_{T_{pl}}$. It is true that from a purely physical point of view the ψ -surface, only exists between the limits $x = 0$ and $x = 1$ (in our case $x > 0$), but from a mathematical point of view we can imagine this surface to extend also beyond those limits²⁾. If we consider a temperature lying above the critical temperatures of the two components of a mixture, then there are, exceptional cases excluded (HARTMAN'S 3^d type), no co-existing phases, that is to say the real ψ -surface does not show a plait, although formula 26 shows that there is a plait-

1) If we take the value of x_{T_k} from the equation (26), insert it in (27) and (28), and finally introduce the k 's, α 's and β 's, the formulae (27) and (28) become KEESOM'S formulae (2b) and (2c) (Comm. n^o. 75), while (26) corresponds to KEESOM'S formula (2a).

2) Outside the limits $x = 0$ and $x = 1$ \downarrow is imaginary owing to the presence of terms with $\log x$ and $\log (1-x)$. Although this is the case the co-existing phases beyond those limits are real, as the co-existence conditions contain the necessarily real expressions $\log \frac{x_2}{x_1}$ and $\log \frac{1-x_2}{1-x_1}$.

point on the imaginary part of it. If the temperature is lower than the critical temperatures of the two components the plait occurs between the limits $x=0$ and $x=1$, but, except for mixtures of the second type, according to formula 26 the plaitpoint lies outside these limits. Hence the case is physically not without significance, but the plaitpoint cannot be observed.

Equation (26) may be written:

$$x_{T_{pl}} = \frac{RT_k k_{11}}{RT_k^2 k_{11} \alpha - m_{01}^2} (T - T_k), \quad \dots \quad (26')$$

and this form shows that $x_{T_{pl}}$ will be positive or negative as $T - T_k$ and $RT_k^2 k_{11} \alpha - m_{01}^2$ have different or the same signs. $RT_k^2 k_{11} \alpha > m_{01}^2$ is only possible if $\alpha < 0$; $RT_k^2 k_{11} \alpha < m_{01}^2$ will always be the case if $\alpha > 0$, but may occur with $\alpha < 0$. The different cases that may occur are shown in the following table.

		$RT_k^2 k_{11} \alpha > m_{01}^2$	
		$\alpha > 0$	$\alpha < 0$
$T > T_k$	$0 > x_{Tk} > x_{T_{pl}}$ figs. 5 and 11	$x_{Tk} > x_{T_{pl}} > 0$ figs. 1 and 7	$x_{T_{pl}} > 0 > x_{Tk}$ figs. 3 and 9
	$x_{T_{pl}} > x_{Tk} > 0$ figs. 6 and 12	$0 > x_{T_{pl}} > x_{Tk}$ figs. 2 and 8	$x_{Tk} > 0 > x_{T_{pl}}$ figs. 4 and 10

7. The border curve in the p, v, x diagram at the temperature T .

Along the border curve $v = v_{Tk} + \Phi \pm \tau$, so that the equation of the border curve may be written

$$0 = (v - v_{Tk})^2 - 2 \Phi (v - v_{Tk}) + \Phi^2 - \varphi^2 \quad \dots \quad (30)$$

where Φ and φ must be replaced by the expressions as functions of p . To the first approximation we can take therefor the expressions (22) and (23) and neglect Φ^2 ; the equation (30) then represents a parabola of the second degree. The apex of this parabola does not, as in the p, v , diagram of a simple substance co-incide with the critical point (p_{Tk} , v_{Tk}), but with the plaitpoint.

Along that parabola

$$\frac{d^2 p}{dv^2} = - \frac{2 m_{01} m_{30} R T_k}{m_{01}^2 + R T_k m_{11}} = - \frac{2 m_{01} k_{30} R T_k}{R T_k^2 k_{11} \alpha - m_{01}^2} \quad \dots \quad (31)$$

This expression is either positive or negative; that is to say that the border curve may be turned with its convex side towards the v -axis, while in the p, v , diagram for a simple substance the border curve is always concave to the v -axis. $\frac{d^2 p}{dv^2}$ will be positive if m and $RT^2_k k_{11} \alpha - m_{01}^2$ have different signs, and will be negative in the other case:

	$RT^2_k k_{11} \alpha > m_{01}^2 \quad \quad RT^2_k k_{11} \alpha < m_{01}^2$	
$m > 0$	figs. 5 and 6	figs. 1—4
$m_{01} < 0$	figs. 11 and 12	figs. 7—10

8. The projection of the connodal line on the x, v plane.

The equation of this curve has been given by KORTEWEG¹⁾. In connection with our preceding formulae it is most easily derived from equation (30) by expressing p in terms of x and v by means of the equation of state (18). I shall now bring it in a form analogous to (30).

The border curve intersects the isothermal of the mixture x at two points (p'_1, v'_1) , and (p'_2, v'_2) which indicate the phases where the condensation begins and ends. I again make:

$$\begin{aligned} \frac{1}{2}(v'_2 + v'_1) - vTk &= \Phi', \quad \frac{1}{2}(v'_2 - v'_1) = \varphi' \\ \frac{1}{2}(p'_2 + p'_1) - pTk &= \Pi' \text{ and } \frac{1}{2}(p'_2 - p'_1) = \pi', \end{aligned}$$

and consider the four infinitely small quantities Φ', φ', Π' and π' as functions of x .

By expressing that the two points are situated on the isothermal (18) and on the border curve (30), I obtain four equations from which the relations we want can be derived. In this way I obtain to the first approximation,

$$\begin{aligned} \Phi' = & -\frac{1}{2m_{30}} \left[\frac{1}{m_{01}} \left(\frac{m_{01}^2}{RT} + m_{11} \right)^2 - \frac{2}{3} \frac{m_{01}^3}{R^2 T^2} + \frac{2}{3} m_{21} - \frac{4m_{40}}{5m_{30}} \left(\frac{m_{01}^2}{RT} + m_{11} \right) \right] x + \\ & + \frac{1}{2m_{30}} \left[\frac{m_{11}}{m_{01}} \left(\frac{m_{01}^2}{RT} + m_{11} \right) + \frac{2}{3} m_{21} - \frac{4m_{11}m_{40}}{5m_{30}} \right] xTk \quad \dots \quad (32) \end{aligned}$$

$$\varphi'^2 = -\frac{1}{m_{30}} \left[\frac{m_{01}^2}{RT} + m_{11} \right] x + \frac{m_{11}}{m_{30}} xTk, \quad \dots \quad (33)$$

$$\Pi' = m_{01}(x - xTk), \quad \dots \quad (34)$$

and

$$\pi' = m_{11}(x - xTk) \varphi'. \quad \dots \quad (35)$$

1) Wien. Ber. 98, 1159, 1889.

Now we may again write for the equation of the connodal line

$$0 = (v - v_{Tk})^2 - 2\Phi'(v - v_{Tk}) + \Phi'^2 - \varphi'^2. \quad (36)$$

To the first approximation along this curve

$$\frac{d^2x}{dv^2} = -\frac{2m_{30}RT_k}{m_{01}^2 + RT_k m_{11}} = \frac{2k_{30}RT_k}{RT_k^2 k_{11} \alpha - m_{01}^2} \quad (37)$$

and this expression has the opposite sign to $RT_k^2 k_{11} \alpha - m_{01}^2$. Here therefore we distinguish only two cases.

1. $RT_k^2 k_{11} \alpha > m_{01}^2$; $\frac{d^2x}{dv^2} < 0$, i. e. the connodal line turns its concave side towards the v -axis (fig. 14);

2. $RT_k^2 k_{11} \alpha < m_{01}^2$; $\frac{d^2x}{dv^2} > 0$ and the connodal line is convex to the v -axis (fig. 15).

9. The critical point of contact.

The characteristic of the critical point of contact is that there the two phases with which the condensation begins and ends coincide.

If x_{Tr} , p_{Tr} and v_{Tr} represent the elements of that point we have there

$$\Phi' = v_{Tr} - v_{Tk}, \quad \varphi' = 0, \quad \Pi' = p_{Tr} - p_{Tk}, \quad \pi' = 0 \text{ and } x = x_{Tr}.$$

and from (33) it follows that

$$x_{Tr} = \frac{RT_k m_{11}}{m_{01}^2 + RT_k m_{11}} x_{Tk}, \quad (38)$$

that is to say to the first approximation the composition at the critical point of contact is the same as at the plaitpoint (cf. 26). The different cases which may occur now follow.

1. $RT_k^2 k_{11} \alpha > m_{01}^2$ (fig. 14).

a). $T > T_k$; x_{Tr} is negative and there is no connodal line inside the region that can be observed. This corresponds to the position of the border curve in figs. 5 and 11.

b). $T = T_k$; $x_{Tr} = 0$ and the formula (30) represents a connodal line which touches the v -axis.

c). $T < T_k$; $x_{Tr} > 0$ and there is a connodal line in the region of positive x , (see also figs. 6 and 12).

2. $RT_k^2 k_{11} \alpha < m_{01}^2$ (fig. 15).

a). $T > T_k$; $x_{Tr} > 0$ and the connodal line lies entirely within the region that can be observed; (figs. 1, 3, 7 and 9).

b). $T = T_k$; $x_{Tr} = 0$ and the connodal line touches the v -axis;

c). $T < T_k$; $x_{Tr} > 0$ and the connodal line can only be completed

by prolonging it in the region of the negative x (fig. 2, 4, 8 and 10).

Equation (34) gives :

$$p_{Tr} = p_{Tk} + m_{01}(x_{Tr} - x_{Tk}) = p_{Tk} - \frac{m_{01}^2}{m_{01}^2 + RT_k m_{11}} x_{Tk}, \quad (39)$$

so that also to the first approximation $p_{Tr} = p_{T_{pl}}$ (comp. equation 27).

And from the equation (32) we derive in connection with (38):

$$v_{Tr} = v_{Tk} + \frac{1}{3} \frac{m_{01}^2}{m_{30}(m_{01}^2 + RT_k m_{11})} \left(m_{21} + \frac{m_{01} m_{11}}{RT_k} \right) x_{Tk}, \quad (40)$$

from which by comparison with (28) we find

$$v_{Tr} - v_{T_{pl}} = \frac{1}{2} \frac{m_{01} m_{11}}{RT_k m_{30}} x_{Tk} = - \frac{1}{2} \frac{k_{11} m_{01}}{RT_k k_{30}} (T - T_k) \quad (41)$$

The difference $v_{Tr} - v_{T_{pl}}$ may be positive or negative, that is to say the critical point of contact may be situated on the vapour or on the liquid branch of the border curve (or of the connodal line). In the first case, as it is well-known, we have retrograde condensation of the first type for all mixtures comprised between x_{Tr} and $x_{T_{pl}}$, in the second case retrograde condensation of the second type :

$T > T_k$	$v_{Tr} < v_{T_{pl}}$; r. c. II; figs. 1, 3 and 5	$v_{Tr} > v_{T_{pl}}$; r. c. I; figs. 7, 9 and 11
$T < T_k$	$v_{Tr} > v_{T_{pl}}$; r. c. I; figs. 2, 4 and 6	$v_{Tr} < v_{T_{pl}}$; r. c. II; figs. 8, 10 and 12

Expressing that the plaitpoint and the critical point of contact lie on the connodal line and subtracting the equations thus obtained we find to the second approximation :

$$x_{Tr} - x_{T_{pl}} = \frac{1}{4} \frac{m_{01}^2 m_{11}^2}{RT_k m_{30} (m_{01}^2 + RT_k m_{11})} x_{Tk}^2; \quad (42)$$

this expression is positive if $RT_k^2 k_{11} \alpha > m_{01}^2$ (fig. 14), and negative if $RT_k^2 k_{11} \alpha < m_{01}^2$ (fig. 15). In the same way we find by means of the border curve

$$p_{Tr} - p_{T_{pl}} = - \frac{1}{4} \frac{m_{01}^3 m_{11}^2}{RT_k m_{30} (m_{01}^2 + RT_k m_{11})} x_{Tk}^2 \quad (43)$$

so that

	$m_{01} > 0$	$m_{01} < 0$
$RT_k^2 k_{11} \alpha > m_{01}^2$	$p_{Tr} < p_{T_{pl}}$; figs. 5 and 6	$p_{Tr} > p_{T_{pl}}$; figs. 11 and 12
$RT_k^2 k_{11} \alpha < m_{01}^2$	$p_{Tr} > p_{T_{pl}}$; figs. 1—4	$p_{Tr} < p_{T_{pl}}$; figs. 7—10

(To be continued).

Physics. — Dr. J. E. VERSCHAFFELT: "*Contributions to the knowledge of VAN DER WAALS' ψ -surface. VII. The equation of state and the ψ -surface in the immediate neighbourhood of the critical state for binary mixtures with a small proportion of one of the components.*" (Continued). Communication n°. 81 from the physical Laboratory at Leiden, by Prof. H. KAMERLINGH ONNES. ¹⁾

(Communicated in the meeting of Sept. 27, 1902).

10. The border curve and the connodal line in special cases.

1. When $m_{01} = 0$, i. e. $p_k \beta = k_{01} T_k a$, all isotherms intersect one another nearly at the critical point (p_{Tk}, v_{Tk}) as we have seen in § 3; according to the equations (26), (27) and (28) the plaitpoint coincides in that case with this critical point. Besides from (31) it follows that

$\frac{d^2 p}{dv^2} = 0$; this value however belongs to $\frac{d^2 p}{dv^2}$ only to the first approximation (i. e. at the critical point itself), or the border curve is a parabola of a higher degree than the second. In fact we find in this case:

$$\Phi = -\frac{1}{2m_{30}} \left(\frac{2}{3} m_{21} - \frac{4}{5} \frac{m_{11} m_{40}}{m_{30}} \right) \Xi, \quad \varphi^2 = -\frac{m_{11}}{m_{30}} \Xi, \text{ and}$$

$$p_1 - p_{Tk} = \left(m_{02} - \frac{1}{3} \frac{m_{11} m_{21}}{m_{30}} \right) \Xi^2;$$

and therefore the border curve to the first approximation becomes a parabola of the fourth degree; the equation of that parabola is:

$$p - p_{Tk} = \frac{m_{30}^2}{m_{11}^2} \left(m_{02} - \frac{1}{3} \frac{m_{11} m_{21}}{m_{30}} \right) (v - v_{Tk})^4.$$

The connodal line, however, remains a parabola of the second degree, on which $\frac{d^2 x}{dv^2} = \frac{2k_{30}}{T_k k_{11} a}$.

2. A second remarkable case is that where $RT_k m_{11} + m_{01}^2 = 0$; for then the term $p_1 - p_{Tk}$ disappears from the expression for φ^2 (equation 23), so that φ becomes of the first order with respect to $p_1 - p_{Tk}$. We then find:

$$\Phi = -\frac{1}{3m_{30}} \left(\frac{m_{01} m_{11}}{RT_k} + m_{21} \right) \frac{p_1 - p_{Tk}}{m_{01}} - \frac{m_{01}}{RT_k m_{30}} \left(\frac{1}{3} m_{11} - \frac{2}{5} \frac{m_{01} m_{40}}{m_{30}} \right) x_{Tk}$$

and

$$\varphi^2 = \frac{m_{11}}{m_{30}} x_{Tk} - \frac{1}{m_{30}} \left(\frac{5}{2} \frac{m_{01} m_{02}}{RT_k} - \frac{1}{3} \frac{m_{01}^2 m_{11}}{R^2 T_k^2 m_{30}} + \right.$$

$$\left. + m_{11} + m_{12} - \frac{2}{3} \frac{m_{01} m_{11} m_{21}}{RT_k m_{30}} - \frac{1}{3} \frac{m_{21}^2}{m_{30}} \right) \left(\frac{p_1 - p_{Tk}}{m_{01}} \right)^2;$$

¹⁾ Comp. Proceedings Royal Acad. of Sciences Sept. 1902.

in the last term I shall express the co-efficient of $(p_1 - p_{Tk})^2$ for convenience by K .

Substituting this in equation (30) we obtain to the first approximation an equation of the second degree, which now no longer represents a parabola but an ellipse or a hyperbola. The coordinates of the centre are:

$$p_c = p_{Tk} \quad \text{and} \quad v_c = v_{Tk} - \frac{m_{01}}{RT_k m_{30}} \left(\frac{1}{3} m_{11} - \frac{2}{5} \frac{m_{01} m_{40}}{m_{30}} \right) x_{Tk},$$

while the straight lines

$$p = p_{Tk} \quad \text{and} \quad v = v_{Tk} + \Phi$$

are conjugate axes. With respect to these axes the coordinates of the border curve are φ and $p_1 - p_{Tk}$, so that the equation of the border curve with respect to those axes is:

$$\varphi^2 - K(p - p_{Tk})^2 = \frac{m_{11}}{m_{30}} x_{Tk} = - \frac{k_{11}}{k_{30}} (T - T_k).$$

In the same case the equation of the connodal line is:

$$\varphi'^2 - K m_{01}^2 (x - x_{Tk})^2 = - \frac{k_{11}}{k_{30}} (T - T_k),$$

with respect to the conjugate axes:

$$x = x_{Tk} \quad \text{and} \quad v = v_{Tk} + \Phi';$$

where Φ' is obtained through substituting $x - x_{Tk}$ for $\frac{p_1 - p_{Tk}}{m_{01}}$ in Φ .

We must now distinguish two cases.

a. $K < 0$; the equations of the border curve and the connodal line represent ellipses. Provided $k_{11} < 0$ and $k_{30} < 0$ these ellipses are real when $T < T_k$; they lie only partially — to the first approximation half — in the real part ($x > 0$) of the ψ -surface. We find two plaitpoints of which only one is in the real ψ -surface and two critical points of contact co-inciding with the plaitpoints (at least to the degree of approximation considered here, i. e. to the order $\sqrt{(T - T_k)}$; the coordinates of these points are:

$$\begin{aligned} x_{Tpl} = x_{Tr} = x_{Tk} \pm \frac{1}{m_{01}} \sqrt{\frac{k_{11}}{K k_{30}}} (T - T_k) \\ p_{Tpl} = p_{Tr} = p_{Tk} \pm \sqrt{\frac{k_{11}}{K k_{30}}} (T - T_k) \\ v_{Tpl} = v_{Tr} = v_c \mp \frac{1}{3 m_{01} m_{30}} \left(\frac{m_{01} m_{11}}{RT_k} + m_{21} \right) \sqrt{\frac{k_{11}}{K k_{30}}} (T - T_k). \end{aligned}$$

If $T = T_k$, the border curve and the connodal line shrink to one point, the critical point of the pure substance; and if $T > T_k$, there is no longer a border curve nor a connodal line.

To this can be added

$$\Pi'' = \frac{1}{2} (p'_2 + p'_1) - p_{xk} = k_{01} (T - T_{xk}) \quad . \quad . \quad . \quad (47)$$

and

$$\pi'' = - \frac{m_{11}}{\alpha T_k} (T - T_{xk}) \varphi'' \quad . \quad . \quad . \quad (48)$$

To the first approximation equation (44) represents a parabola, of which the apex determines the elements of the critical point of contact for the mixture x . For we know that in the case of the critical point of contact $v'_2 = v'_1 = v_{xr}$, so that $\varphi'' = 0$ and $\Phi'' = v_{xr} - v_{xk}$. Hence it follows that¹⁾:

$$T_{xr} = T_{xk} - \frac{m_{01}^2}{RT_k k_{11}} x \quad . \quad . \quad . \quad . \quad (49)$$

$$p_{xr} = p_{xk} - \frac{k_{01} m_{01}^2}{RT_k k_{11}} x \quad . \quad . \quad . \quad . \quad (50)$$

$$v_{xr} = v_{xk} + \left[m_{01}^2 v_k (\alpha - \beta) + \frac{1}{3} \frac{m_{01}^2}{m_{30}} \left(\frac{m_{01} m_{11}}{RT_k} + m_{21} \right) \right] \frac{x}{RT_k m_{11}} \quad . \quad (51)$$

In order to derive from this the equation of the border curve in the p, v, T -diagram, we must express T in terms of p and v by means of equation (13).

Then we find:

$$0 = (v - v_{xk})^2 - 2 \Phi''' (v - v_{xk}) + \Phi'''^2 - \varphi'''^2 \quad . \quad . \quad . \quad (52)$$

where

$$\begin{aligned} \Phi''' = & - \frac{1}{2m_{30}} \left[\frac{m_{01}}{RT_k} \left(\frac{m_{01}^2}{RT_k} + m_{11} \right) - \frac{2}{3} \frac{m_{01}^3}{R^2 T_k^2} - \frac{4}{5} \frac{m_{40}}{m_{30}} \frac{m_{01}^2}{RT_k} \right] x + \\ & + \frac{v_k (\alpha - \beta)}{k_{01} \alpha T_k} (p - p_{xk}) + \frac{1}{2k_{01} m_{30}} \left[\frac{m_{11}}{m_{01}} \left(\frac{m_{01}^2}{RT_k} + m_{11} \right) + \frac{2}{3} m_{21} - \frac{4}{5} \frac{m_{11} m_{40}}{m_{30}} - \right. \\ & \left. - \frac{k_{11} m_{11}}{k_{01}} \right] \frac{p - p_{xk}}{\alpha T_k} \quad . \quad . \quad . \quad . \quad (53) \end{aligned}$$

and

$$\varphi'''^2 = - \frac{m_{01}^2}{RT_k m_{30}} x + \frac{m_{11}}{k_{01} m_{30}} \frac{p - p_{xk}}{\alpha T_k} \quad . \quad . \quad . \quad . \quad (54)$$

To a first approximation (52) is a parabola on which

$$\frac{d^2 p}{dv^2} = 2 \frac{k_{01} m_{30}}{m_{11}} \alpha T_k = - 2 \frac{k_{01} k_{30}}{k_{11}}$$

as in the case of the border curve of the pure substance.

The apex of the border curve is the point of the maximum co-existence

¹⁾ We obtain the same formulae if we replace in equation (26) xT_k by its value (17), put $T = T_{xr}$ and $xT_r = x$, solve T_{xr} and substitute it in (39) and (40).

pressure ¹⁾. Let p_{xm} , v_{xm} , T_{xm} , be its coordinates, then we find by putting $\varphi''' = 0$ and $\Phi''' = v_{xm} - v_{xk}$

$$p_{xm} = p_{xk} - \frac{k_{01} m_{01}^2}{RT_k k_{11}} x \quad . \quad . \quad . \quad . \quad . \quad (55)$$

$$v_{xm} - v_{xk} + \left[m_{01}^2 v_k (\alpha - \beta) + \frac{1}{3} \frac{m_{01}^2}{m_{80}} \left(m_{21} + \frac{m_{01} m_{11}}{RT_k} - \frac{3 k_{11} m_{11}}{2 k_{01}} \right) \right] \frac{x}{RT_k m_{11}} \quad (56)$$

$$T_{xm} = T_{xk} - \frac{m_{01}^2}{RT_k k_{11}} x \quad . \quad . \quad . \quad . \quad . \quad (57)$$

Hence to the first approximation $p_{xm} = p_{xr}$ and $T_{xm} = T_{xr}$, but

$$v_{xm} - v_{xr} = - \frac{1}{2} \frac{m_{01}^2 k_{11}}{RT_k k_{01} k_{80}} x; \quad . \quad . \quad . \quad . \quad . \quad (58)$$

for real mixtures, that is to say $x > 0$, the latter expression is necessarily negative, so that the critical point of contact is always situated on the descending (right) branch of the border curve. We cannot call it the vapour branch, because here the apex of the border curve is not the plaitpoint as in the p, v, x -diagram. The critical point of contact is situated thus, because the critical isothermal touches the border curve at that point, and because on that isothermal and hence also at the critical point of contact $T_{xr} > T_{xk}$ (at least for real mixtures), therefore $\frac{\partial p}{\partial v} < 0$ for the border curve. This corresponds to a diagram-

matical representation of a p, v, T -diagram for a mixture given by KUENEN ²⁾ and also with the experimental diagram for the mixture: 0.95 carbon dioxide, 0.05 hydrogen which I have given in my thesis for the doctorate. In spite of the small value of x , terms of higher order appear to have such a great influence in the case of this mixture that the apex of the border curve lies far outside the area investigated, and the border curve at the critical point of contact is no longer concave towards the v -axis but convex.

The plaitpoint elements for the mixture of composition x are found by substituting T_{xpl} for T and x for x_{Tpl} in equation (26), by solving T_{xpl} and substituting that value in (27) and (28). Then we find

$$T_{xpl} = T_k \left[1 + \frac{m_{01}^2 + RT_k m_{11}}{RT_k m_{11}} \alpha x \right] = T_{xk} - \frac{m_{01}^2}{RT_k k_{11}} x \quad . \quad . \quad (59)$$

$$p_{xpl} = p_k + \left[p_k \beta + \frac{k_{01} m_{01}^2}{R m_{11}} \alpha \right] x = p_{xk} - \frac{k_{01} m_{01}^2}{RT_k k_{11}} x \quad . \quad . \quad (60)$$

¹⁾ Comp. HARTMAN, *Journ. Phys. Chem.*, 5, 437, 1901. Communications Leiden Suppl. N° 3 p. 14.

²⁾ *Zeitschr. f. physik. Chem.*, XXIV, 672, 1897.

$$v_{xpl} = v_{xk} + \left[m_{01}^2 v_k (\alpha - \beta) + \frac{m_{01}}{2m_{80}} \left(\frac{2}{3} m_{01} m_{21} - \frac{1}{3} \frac{m_{01}^2 m_{11}}{RT_k} - m_{11}^2 \right) \right] \frac{x}{RT_k m_{11}}, \quad (61)$$

which formulae, after some reductions, can be put in the form in which KEESOM has given them (*Comm.*, n°. 75). Also the following well known equation ¹⁾ results directly from equations (59) and (60)

$$p_{xpl} - p_{xk} = k_{01} (T_{xpl} - T_{xk}) \quad . \quad . \quad . \quad . \quad . \quad (62)$$

which also according to equations (49), (50), (55) and (57) holds for the coordinates of the critical point of contact and for the apex of the border curve.

From the coordinates of the plaitpoint of mixtures of carbon dioxide with a small proportion of hydrogen ²⁾ ($x = 0, 0,05$ and $0,1$) I derive the following formulae

$$\left. \begin{aligned} T_{xpl} &= T_k (1 - 0,30 x + x^2) \\ p_{xpl} &= p_k (1 + 4,4 x + 11 x^2) \\ v_{xpl} &= v_k (1 - 0,40 x - 8 x^2) \end{aligned} \right\} \quad . \quad . \quad . \quad . \quad (63)$$

In connection with the formulae (16) I obtain directly from these :

$$\frac{p_{xpl} - p_{xk}}{T_{xpl} - T_{xk}} = 1,66 (1 + 2x),$$

in good harmony with equation (62) ($k_{01} = 1,61$) ³⁾. Using the value $k = -513$ ⁴⁾, I moreover find that the formulae (59) and (60) applied to mixtures of carbon dioxide and hydrogen become :

$$T_{xpl} = T_k (1 + 0,03 x) \quad \text{and} \quad p_{xpl} = p_k (1 + 6,4 x); \quad . \quad (63')$$

hence the agreement with the formulae (63) is decidedly bad, as has also been remarked by KEESOM (*loc. cit.*, p. 13). We cannot, however, draw any conclusions from this; it is improbable that the inaccuracy of the data should cause this great deviation; but from the fact that terms of higher order produce such a great influence in the mixture $x = 0,05$, we see that quadratic formulae are very unfit for this comparison ⁵⁾, the more so as it appears from

¹⁾ Comp. v. D. WAALS, *Versl. Kon. Akad.*, Nov. 1897. It also follows directly from the equation of state (13) in connection with (15), by expressing that the elements of the plaitpoint satisfy this equation and by neglecting terms of a higher order than the first.

²⁾ VERSCHAFFELT, Thesis for the doctorate, Leiden 1899.

³⁾ Comp. also KEESOM, *loc. cit.*, p. 14.

⁴⁾ Derived from $\frac{RT_k}{p_k v_k} \frac{\partial^2 \pi}{\partial \omega \partial \tau} = -32,2$ (KEESOM, p. 12).

⁵⁾ By introducing the values for $x = 0,2$ (comp. VERSCHAFFELT, *Arch. Néerl.*, (2), 5, 649 etc., 1900, Comm. n°. 65, and KEESOM, *loc. cit.* p. 12) they certainly will not become better.

KEESOM's calculations (p. 13) that tolerably small variations in the values of α and β greatly influence the values of $\frac{dT_{xpl}}{dx}$ and $\frac{dp_{xpl}}{dx}$.

Accurate observations for mixtures with still smaller compositions are therefore highly desirable. As the v_{xpl} , and also the coordinates of the critical plaitpoint, are known with less certainty than the T_{xpl} and p_{xpl} , a comparison of the theoretical and the experimental values for these quantities is practically useless.

Again from the preceding equations $p_{xpl} = p_{xr}$, $T_{xpl} = T_{xr}$ to a first approximation, and

$$v_{xpl} - v_{xr} = -\frac{1}{2} \frac{m_{01}}{RT_k m_{s_0}} \left(\frac{m_{01}^2}{RT_k} + m_{11} \right) x \quad . \quad . \quad . \quad (64)$$

Hence the plaitpoint may lie either to the right or to the left of the critical point of contact; for positive x we have

	$m_{01} > 0$	$m_{01} < 0$
$RT_k^2 k_{11} \alpha > m_{01}^2$	$v_{xpl} < v_{xr}$; r. c. I	$v_{xpl} > v_{xr}$; r. c. II
$RT_k^2 k_{11} \alpha < m_{01}^2$	$v_{xpl} > v_{xr}$; r. c. II	$v_{xpl} < v_{xr}$; r. c. I

If the plaitpoint lies to the left of the critical point of contact, it may still lie either to the right or to the left of the apex, that is to say either on the descending or on the ascending branch of the border curve. In fact, according to (58) and (64) it lies:

1. to the right of the critical point of contact when m_{01} and $\frac{m_{01}^2}{RT_k} + m_{11}$ have the same signs,

2. between the critical point of contact and the apex when $\frac{k_{01}}{k_{11}} \left(\frac{m_{01}^2}{RT_k} + m_{11} \right) > m_{01} > 0$ or $0 > m_{01} > \frac{k_{01}}{k_{11}} \left(\frac{m_{01}^2}{RT_k} + m_{11} \right)$, and

3. to the left of the apex when $m_{01} > \frac{k_{01}}{k_{11}} \left(\frac{m_{01}^2}{RT_k} + m_{11} \right) > 0$ or $0 > \frac{k_{01}}{k_{11}} \left(\frac{m_{01}^2}{RT_k} + m_{11} \right) > m_{01}$.

In the p, v, T -diagram the plaitpoint has no geometrical meaning.

The expression that the coordinates of the critical point of contact and the plaitpoint satisfy the equation (44) gives, to the second approximation:

$$T_{xpl} - T_{xr} = -\frac{1}{4} \frac{m_{01}^2}{RT_k k_{s_0} k_{11}} \left(\frac{m_{01}^2}{RT_k} + m_{11} \right)^2 x^2 \quad . \quad . \quad . \quad (65)$$

The right side is necessarily negative and therefore we always have $T_{xr} > T_{xpl}$, which also necessarily follows from the meaning of the critical point of contact. In the same way we find by means of equation (52):

$$p_{xpl} - p_{xr} = \frac{1}{2} \frac{k_{01}}{k_{11}} \frac{m_{01}^2}{RT_k k_{30}} \left(\frac{m_{01}^2}{RT_k} + m_{11} \right) \left[\frac{m_{01} k_{11}}{k_{01}} - \frac{1}{2} \left(\frac{m_{01}^2}{RT_k} + m_{11} \right) \right] x^2. \quad (66)$$

12. The condensation.

The line which indicates the relation between the pressure and the volume during the condensation, the so-called experimental isothermal, extends between the two points p'_1, v'_1 and p'_2, v'_2 (the points where the condensation begins and ends) but we can also imagine it to extend beyond those two points, although there it has only a mathematical meaning; for beyond those two points the quantity of one of the phases would be negative. In order to find the equation of the experimental isothermal we must seek at each volume for the pressure at which the two phases into which the mixture splits, can co-exist. For this purpose I return to the projection on the x, v -plane (§ 8) of the ψ -surface belonging to the temperature T . If v_1, x_1 and v_2, x_2 are the phases into which the mixture x splits when the volume v is reached ($v_2 > v > v_1$), the point v, x lies on the straight line connecting the points v_1, x_1 and v_2, x_2 and hence we have this relation:

$$\frac{v - vTk - \Phi}{x - xTk - \Xi} = \frac{\varphi}{\xi}, \quad . \quad . \quad . \quad . \quad . \quad (67)$$

where Φ, Ξ, φ and ξ have the same meaning as in § 5. If p_1 is the pressure at which the two phases x_1 and x_2 co-exist then we obtain the equation of the experimental isothermal by expressing the quantities Φ, Ξ, φ and ξ of equation (67) in p_1 by means of the equations (22), (23), (24) and (25).

That this experimental isothermal passes through the two points v'_1, x and v'_2, x follows directly from the way in which its equation has been derived; we also obtain it from the substitution of v'_1, x'_1 — or v'_2, x'_2 — for v, x , which involves the substitution of v'_1, x'_1 for v_1, x_1 — or of v'_2, x'_2 for v_2, x_2 .

By successive approximations (67) is brought to the form:

$$p_1 = pTk + m_{01}(x - xTk) - \frac{m_{01}^2}{RT_k}(v - vTk)x + \dots; \quad . \quad . \quad (68)$$

if we consider only the three first terms, this is the equation of a straight line, hence of that connecting the two phases where the condensation begins and ends. In connection with (18) we find, neglecting terms of higher order,

$$p - p_1 = m_{11} (v - v_{Tk}) (x - x_{Tk}) + \frac{m_{01}^2}{RT_k} (v - v_{Tk})^2 x + m_{00} (v - v_{Tk})^3,$$

and according to (33) this may be written

$$p - p_1 = k_{00} (v - v_{Tk}) [(v - v_{Tk})^2 - \varphi'^2].$$

We see that in this form the experimental isothermal intersects the theoretical at three points¹⁾, viz. $v = v_{Tk} + \varphi'$, $v = v_{Tk} - \varphi'$ and $v = v_{Tk}$ (all to the first approximation); the two first points are the points at which condensation begins and ends (φ' has been neglected as being of higher order than φ'), the third lies between the two first.

When $v_{Tk} + \varphi' > v > v_{Tk}$, that is to say at the beginning of the condensation, $p > p_1$ and the theoretical isothermal lies above the experimental; when $v_{Tk} > v > v_{Tk} - \varphi'$, i.e. at the end of the condensation, $p > p_1$ and the experimental isothermal is the higher²⁾; this, indeed, follows necessarily from the *s*-shape of the theoretical isothermal, and the approximate straightness of the experimental.

According to thermodynamics the two areas enclosed by the theoretical and the experimental isothermal must be equivalent³⁾, that is to say:

$$\int_{v_1}^{v_2} (p - p_1) dv = 0.$$

or

$$\int_{-\varphi'}^{+\varphi'} (p - p_1) d(v - v_{Tk}) = 0,$$

and this actually follows from the form, found just now for $p - p_1$.

This has only been proved for the terms considered here; but obviously it must also be possible to prove this for terms of higher order.

13. The p , T diagram.

a. The vapour pressure curve of the pure substance. We have found to a first approximation:

$$p_1 = p_k + k_{01} (T - T_k).$$

As k_{01} is positive, this straight line rises and terminates at the

¹⁾ Comp. for this HARTMAN, Comm., n°. 56 and Suppl. n°. 3 p. 25; Journ. Phys. Chem., 5, 450, 1901.

²⁾ Here the proof is only given for mixtures with small composition. For a general proof comp. KUENEN, Zeitschr. f. Physik. Chem., XLI, 46, 1902.

³⁾ It has escaped BLÜMCKE's notice, who mentions this theorem in 1890 (Zeitschr. f. physik. Chem., VI, p. 157) that it occurs already in a treatise of VAN DER WAALS of 1880 (Verh. Kon. Akad., Bd. 20, p. 23).

point p_k , T_k . T_k is a maximum temperature, so that this curve lies in the third quadrant ($S'O$, fig. 16.)

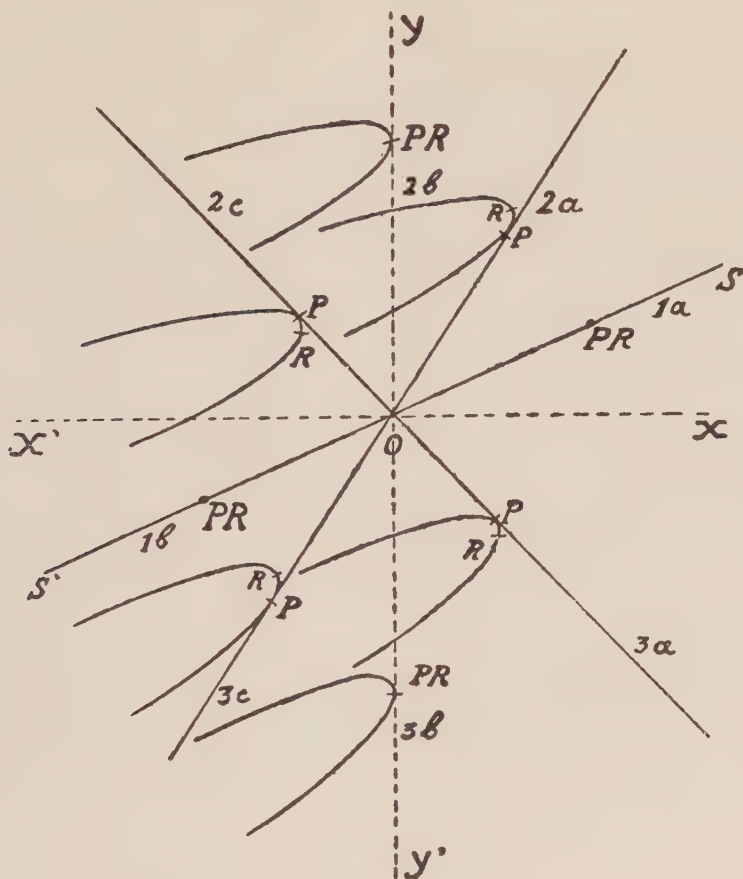


Fig. 16.

b. The plaitpoint curve. According to equation (27)

$$p_{T_{pl}} = p_k + \left[p_k \beta - \frac{m_{01}^3}{m_{01}^2 + RT_k m_{11}} \right] \frac{T - T_k}{\alpha T_k} = p_k + \left(k_{01} - \frac{RT_k k_{11} m_{01}}{m_{01}^2 + RT_k m_{11}} \right) (T - T_k)$$

This curve may have all possible directions. If we consider only real mixtures ($x > 0$), it extends only on one side of the point p_k , T_k , namely that corresponding to such values that $T - T_k$ and $m_{01}^2 + RT_k m_{11}$ have the same signs (according to equation 26').

With regard to the position of the plaitpoint curve we distinguish the following cases :

1. $m_{01} = 0$. $p_{T_{pl}} = p_k + k_{01} (T - T_k)$, hence the beginning of the plaitpoint curve will lie either in the direction of the vapour pressure

curve of the pure substance or will co-incide with it as $T > T_k$ or $T < T_k$, that is to say, according to (26'), as α is positive or negative. In the first case (1a), therefore, the plaitpoint curve will lie in the first quadrant (*OS* fig. 16), in the second case (1b) in the third quadrant (*OS'*). We have noted that then the plaitpoint elements of a mixture co-incide with the critical elements which the mixture would have, if it remained homogeneous, hence the mixture behaves like a pure substance. This is the case $\frac{\partial^2 \psi}{\partial x \partial v} = 0$ already discussed by VAN DER WAALS¹⁾; in this case there is a mixture — here it must be the pure substance itself — for which the vapour tension is a maximum or a minimum, and indeed it follows from the expression for $p_1 - p_{1k}$ in this case²⁾ that $\left(\frac{\partial p_1}{\partial x_1}\right)_{x_1=0} = 0$.

2a. $m_{01} > 0$ and $m_{01}^2 + RT_k m_{11} > 0$. $\frac{dp_{T_{pl}}}{dT} > k_{01}$ so that the plaitpoint curve lies in the angle *SOY* because $T - T_k$ must be also positive.

2b. $m_{01} > 0$ and $m_{01}^2 + RT_k m_{11} = 0$, $\frac{dp_{T_{pl}}}{dT} = \pm \infty$, and the beginning of the plaitpoint curve co-incides with *OY'*.

Thus we have here the second special case of the shape of the plaitpoint curve investigated by VAN DER WAALS, i. e. where there is a maximum or minimum temperature, here the critical temperature of the pure substance. Really in this case (§ 10,2), as $p_{T_k} - p_k$ is of higher order than $p_{T_{pl}} - p_k$,

$$T - T_k = \frac{Kk_{30}}{k_{11}} (p_{T_{pl}} - p_k)^2$$

hence $\left(\frac{dT_{pl}}{dp_{T_{pl}}}\right)_k = 0$. $T > T_k$, that is to say T_k is the minimum plaitpoint temperature, when $K > 0$; this is the case where the border curve and the connodal line are hyperbolae (mixtures of HARTMAN's third type). And $T < T_k$, that is to say T_k is a maximum, when $K < 0$; in this case the border curve and the connodal line are ellipses (mixtures of the second type).

2c. $m_{01} > 0$ and $m_{01}^2 + RT_k m_{11} < 0$. $\frac{dp_{T_{pl}}}{dT} < k_{01}$, and because

¹⁾ Arch. Néerl., (1), 30, 266, 1896.

²⁾ Comp. preceding communication, p. 267; to the first approximation $\Xi = x_1$.

³⁾ Not with *OY'*, for, as in this case $p_{T_k} - p_k$ and x_{T_k} are infinitely small with respect to $p_{T_{pl}} - p_k$ and $x_{T_{pl}}$ (§ 10,2), according to (29) $p_{T_{pl}} - p_k = m_{01} x$, so that for $x > 0$, $p_{T_{pl}} > p_k$.

$T - T_k$ must also be negative the plaitpoint curve lies in the angle $S'OY$.

3a. $m_{01} < 0$ and $m_{01}^2 + RT_k m_{11} > 0$, $\frac{dp_{rpl}}{dT} < k_{01}$, but $T - T_k > 0$, and hence in the angle SOY' .

3b. $m_{01} < 0$ and $m_{01}^2 + RT_k m_{11} = 0$. The plaitpoint curve touches OY'^1). Compare moreover 2b.

3c. $m_{01} < 0$ and $m_{01}^2 + RT_k m_{11} < 0$. $\frac{dp_{rpl}}{dT} > k_{01}$, but $T - T_k > 0$, hence in the angle $S'OY'$.

From this it appears that $\frac{dp_{rpl}}{dT}$ can take all possible values. According to VAN DER WAALS²⁾, however, this is not true and the case $\frac{dp_{rpl}}{dT} = \frac{pk}{T_k}$ for instance could never occur. But it should be borne in mind that this rule of VAN DER WAALS does not rest on an exclusively thermodynamic reasoning, but also on special suppositions about the form of the equation of state, which naturally corresponds to special relations between the co-efficients introduced here, and as a matter of course it is always possible that the numerical values of the coefficients are such, that one or more of the cases considered are excluded.

c. *The critical point of contact curve.* To the first approximation $p_{Tr} = p_{Tpl}$, so that the critical point of contact curve to a first approximation co-incides with the plaitpoint curve and the considerations in b hold also for this line. Equation (43) shows moreover that to a second approximation:

$$p_{Tr} - p_{Tpl} = -\frac{1}{4} \frac{m_{01}^3 k_{11}^2}{RT_k m_{30} (m_{01}^2 + RT_k m_{11})} (T - T_k)^2,$$

from which it follows that the critical point of contact curve lies above the plaitpoint curve when m_{01} and $m_{01}^2 + RT_k m_{11}$ have the same signs; this occurs in the cases 2a and 3c just mentioned, hence in the angles SOY and $S'OY'$. In the other cases the point of contact curve is the lower. Moreover the two curves also co-incide to a second approximation if $m_{01} = 0$ and even if $m_{01}^2 + RT_k m_{11} = 0$. $\left(\frac{dp_{rpl}}{dT} = \frac{dp_{Tr}}{dT} = \pm \infty \right)$ although in that case $p_{Tr} - p_{Tpl}$ is not zero to the second approximation.

d. *The border curves.* This position of the critical point of con-

¹⁾ $p_{rpl} < p_k$ for $x > 0$; comp. preceding note.

²⁾ Arch. Néerl., (2), 2, 79, 1898.

fact curve with respect to the plaitpoint curve corresponds to the position of the critical point of contact with respect to the plaitpoint on the border curves, represented in an exaggerated way in fig. 16. To the second approximation those border curves are parabolae which touch the plaitpoint curve and have a vertical tangent at the critical point of contact, but to the first approximation they co-incide with the axis which is conjugate to the vertical chords and the equation of which according to (47), is :

$$p = p_{xk} + k_{01} (T - T_{xk}) = p_{xpl} + k_{01} (T - T_{xpl}).$$

Hence these straight lines are parallel with the vapour pressure curve of the pure substance and terminate, on the plaitpoint curve, in the plaitpoint of the mixture to which they belong.

14. Continuation of § 9: the critical point of contact.

Mr. KEESOM kindly informs me that the method given by him in Comm. N°. 75 and which leads very easily to the constants of the plaitpoint presents difficulties when applied to determine the constants of the critical point of contact.

He however succeeded, by means of the method used by me in § 9, in deriving the constants of the critical point of contact from the formulæ¹⁾, given by KORTEWEG in his paper "Ueber Faltenpunkte", Wien. Sitz. Ber. Bd. 98, p. 1154, 1889, and proceeded thus.

It has been shown in Comm. N°. 59^b, p. 36²⁾ that instead of deducing the coexistence-conditions by rolling the tangent-plane over the ψ -surface, we can also obtain them by rolling the tangent-plane over a ψ' -surface, the latter being deduced from the ψ -surface by making the distance, measured in the direction of the ψ -axis, between this surface and a fixed tangent-plane the third coordinate perpendicular to x and v . We can go a step further in this direction by deducing a ψ'' -surface by means of KORTEWEG's projective transformation³⁾

$$\psi'' = \psi' - v' \left(\frac{\partial \psi'}{\partial v'} \right)_{pl} - x' \left(\frac{\partial \psi'}{\partial x'} \right)_{pl}$$

$$x'' = x' - m v'$$

$$v'' = v'$$

Here

$$\psi' = \psi - \psi_{T_{pl}}$$

$$x' = x - x_{T_{pl}}$$

$$v' = v - v_{T_{pl}}$$

¹⁾ The simplest way of proving that the case $c_1 = \infty$ in KORTEWEG's formula (4) does not influence the present deduction, is by noting that the area over which the development is applied is infinitely small in comparison with $x_{T_{pl}}$.

²⁾ Proceedings Sept. 1900, p. 296.

³⁾ See KORTEWEG l. c. equation 38.

As

$$\left(\frac{\partial \psi''}{\partial x''}\right)_1 = \left(\frac{\partial \psi''}{\partial x''}\right)_2$$

$$\left(\frac{\partial \psi''}{\partial v''}\right)_1 = \left(\frac{\partial \psi''}{\partial v''}\right)_2$$

$$\psi_1'' - x_1'' \left(\frac{\partial \psi''}{\partial x''}\right)_1 - v_1'' \left(\frac{\partial \psi''}{\partial v''}\right)_1 = \psi_2'' - x_2'' \left(\frac{\partial \psi''}{\partial x''}\right)_2 - v_2'' \left(\frac{\partial \psi''}{\partial v''}\right)_2$$

when

$$\left(\frac{\partial \psi'}{\partial x'}\right)_1 = \left(\frac{\partial \psi'}{\partial x'}\right)_2, \text{ etc.}$$

it is also possible to obtain the coexisting phases by rolling a tangent-plane over this ψ'' -surface. ψ'' as function of x'' and v'' presents the form

$$\psi'' = c_1 x''^2 + d_3 x'' v''^2 + e_5 v''^4 \quad (\text{KORTEWEG's equation 4}).$$

Hence for the connodal curve KORTEWEG's deduction may be applied, and we find for the equation of that curve

$$x'' = -2 \frac{e_5}{d_3} v''^2 \quad (\text{equation 8 l. c.}).$$

m is now found from

$$m \left(\frac{\partial^2 \psi}{\partial x^2}\right)_{eT} + \left(\frac{\partial^2 \psi}{\partial x \partial v}\right)_T = 0 \quad (\text{equation 34}),$$

where the differential quotients are taken for the plaitpoint, so that for a substance with a small proportion of one component, to the first approximation

$$m = \frac{1}{MRT_k} \left(\frac{\partial p}{\partial x}\right)_{vT} x_{TPl}.$$

Further we may put, leaving out terms of higher order, according to equation (39)

$$d_3 = -\frac{1}{2MRT_k} \left\{ \left(\frac{\partial p}{\partial x}\right)_{vT}^2 + MRT_k \left(\frac{\partial^2 p}{\partial x \partial v}\right)_T \right\}$$

$$e_5 = -\frac{1}{24} \left(\frac{\partial^3 p}{\partial v^3}\right)_{xT}.$$

Using the property that for the point of contact $\frac{dx}{dv} = 0$, this yields:

$$v_{Tl} - v_{TPl} = 3 \frac{\left(\frac{\partial p}{\partial x}\right)_{vT}}{(MRT_k)^2 \left(\frac{\partial^3 p}{\partial v^3}\right)} \left\{ \left(\frac{\partial p}{\partial x}\right)_{vT}^2 + MRT_k \left(\frac{\partial^2 p}{\partial x \partial v}\right)_T \right\} x_{TPl}$$

and

$$x_{Tr} - x_{Tpl} = \frac{3}{2} \frac{\left(\frac{\partial p}{\partial x}\right)_{vT}^2}{(MRT_k)^3 \frac{\partial^3 p}{\partial v^3}} - \left\{ \left(\frac{\partial p}{\partial x}\right)_{vT}^2 + MRT_k \left(\frac{\partial^2 p}{\partial x \partial v}\right) \right\} x^2_{Tpl}.$$

So that for $x=0$: $\frac{dx_{Tr}}{dT} = \frac{dx_{Tpl}}{dT}$, or $\frac{dT_{xr}}{dx} = \frac{dT_{xpl}}{dx}$, from which we easily derive that also $\frac{dp_{xr}}{dx} = \frac{dp_{xpl}}{dx}$ so that in the pT -diagram the point of contact curve and the plaitpoint curve touch at the ends. We find further that with the same x :

$$T_{xr} - T_{xpl} = \frac{3}{2} \frac{\left(\frac{\partial p}{\partial x}\right)_{vT}^2}{(MRT_k)^4 \left(\frac{\partial^3 p}{\partial v^3}\right) \left(\frac{\partial^2 p}{\partial v \partial T}\right)} \left\{ \left(\frac{\partial p}{\partial x}\right)_{vT}^2 + MRT_k \left(\frac{\partial^2 p}{\partial x \partial v}\right)_T \right\} x^2.$$

from which $p_{xr} - p_{xpl}$ can be easily found.

If, as in Communication N^o. 75 (Proceedings Nov. 1901), we introduce the law of corresponding states, we find:

$$v_{Tr} - v_{Tpl} = 3 C_4 v_k \frac{\beta - \alpha \left(\frac{\partial \pi}{\partial \tau}\right)}{C_4^3 \left(\frac{\partial^3 \pi}{\partial \omega^3}\right)} \left[\left\{ \beta - \alpha \left(\frac{\partial \pi}{\partial \tau}\right) \right\}^2 - C_4 \alpha \left(\frac{\partial^2 \pi}{\partial \omega \partial \tau}\right) \right] x$$

$$T_{xr} - T_{xpl} = \frac{3}{2} \frac{\left\{ \beta - \alpha \left(\frac{\partial \pi}{\partial \tau}\right) \right\}^2}{C_4^3 \left(\frac{\partial^3 \pi}{\partial \omega^3}\right) \cdot C_4 \left(\frac{\partial^2 \pi}{\partial \omega \partial \tau}\right)} \left[\left\{ \beta - \alpha \left(\frac{\partial \pi}{\partial \tau}\right) \right\}^2 - C_4 \alpha \left(\frac{\partial^2 \pi}{\partial \omega \partial \tau}\right) \right] x^2.$$

Physiology. — "*On the structure of the light-perceiving cells in the spinal cord, on the neurofibrillae in the ganglioncells and on the innervation of the striped muscles in amphioxus lanceolatus.*"

By Dr. J. BOEKE. (Communicated by Prof. T. PLACE).

In connection with a former note ¹⁾ I mean to describe here some points of the histology of the central and peripheral nervous system of *amphioxus lanceolatus*, especially to follow the neurofibrillae in their arrangement and distribution in the cells and in the muscle-plates.

This paper is the outcome of observations begun in 1900 in the Stazione Zoologica at Naples, but then not carried any farther, to study the structure of the pigmented cells of the spinal cord. During

¹⁾ Proceedings of the Royal Academy of Amsterdam. Meeting of April 19, 1902.

a stay at the Zoological Laboratory of Prof. ST. APÁTHY in Kolozsvár once again I took up the theme, with some excellently fixed material I got through Prof. APÁTHY's kindness. Finally the researches were carried on in the Histological Laboratory of Amsterdam.

A. The structure of the light-perceiving cells (eye-cells).

In 1898 HESSE¹⁾ showed, that the peculiar pigmented cells, which are found in the spinal cord grouped round the ventral wall of the central canal, and which after beginning at the third segment, are arranged segmentally through the whole medulla, are each of them composed of two cells, one of them a big ganglioncell without pigment, the other a cupshaped cell, filled up entirely with dark brown pigmentgrains; the last cell covering the greater part of the firstnamed cell and hiding it from view.

The big unpigmented cells HESSE called eye-cells, light-perceiving cells, the cupshaped pigmented cells he called the pigmentcup (Pigmentbecher), and the whole complex he compared with the cupshaped eyes of the Planarians, that are equally composed of two cells, and attributed to it the function of light-perception.

The arrangement of these two-celled eyes in the spinal cord is strictly segmental. They begin in the fourth segment, with two eyes; from there each segment is furnished with about 25 eyes. In the region of the tail the number lessens, until a segment has only one eye or none at all.

The eyes lying ventrally of the central canal are always looking down, their line of vision, if we may call it so, being directed to the ventral side of the animal, those at the left side of the central canal look upward and to the right, those at the right side look down and to the right.

The pigmentcup consists of one cell, the nucleus, when distinguishable, lying at the concave side of the cup.

The eye-cell is coneshaped, the base being covered by the pigmentcup, the top being drawn out into a thin process. At the basal side (turned towards the pigmentcup) the protoplasm is differentiated into a layer of fine small rods, placed at right angles to the cell-periphery, and continuing in the protoplasm as a network of very thin fibres. Another layer of minute rods may be seen close against the pigmentcup. Between those two layers a clear space is formed, which is not caused by a shrinking of the cell.

W. KRAUSE¹⁾ did not agree with the results of HESSE. He still maintained that the pigmented cells in the spinal cord consisted

¹⁾ Zeitschr. f. Wiss. Zoologie. Bd. 63. 1898. p. 456.

¹⁾ Anat. Anzeiger. Bd. 14. Pag. 470. Zool. Anzeiger. Bd. 21. p. 481.

each of them of only one cell with the pigmentgrains lying only at the periphery, just as HELJMANS and v. D. STRICHT ¹⁾ had said in 1898; by BEER ²⁾ and SCHNEIDER ³⁾ the description given by HESSE was taken for right and confirmed.

As to the arrangement of the pigmentcells in the spinal cord in the first place, the observations of HESSE are not complete. They do not simply lessen in number going from before backwards. In young pelagic larvae there are to be seen very distinctly two groups of pigmentcells, one in the cranial part of the body, the other in the caudal half. Between those groups there are much less pigmentcells in each segment. In later stages however these two groups become fused, and then the arrangement is in the main as it is described by HESSE.

As regards the position occupied by the pigmentcap on the eye-cell, I can in the main confirm the observations of HESSE. The eyes at the ventral side of the central canal are always looking down, those at the left are mostly looking upwards and to the right, those at the right mostly downwards and to the right.

The histological structure of the eyes seems to me to be slightly different from the one described by HESSE and SCHNEIDER.

The nucleus of the pigment-cell is never lying at the concave, but mostly at the convex side of the cupshaped cell; sometimes the nucleus is found in the middle of the pigment-cell, where often a clear pigmentfree zone of protoplasm may be distinguished. According to HESSE the pigment-cup consists always of only one cell. Now sometimes in young animals, where the pigment is of a light-brown colour and the nucleus may therefore be seen very clearly, I found two nuclei in the pigment-cap, and so it seems to me that there are sometimes two pigment-cells with one eye-cell. So the form of the pigment-cap in fig. 3 seems also to point to the pigment-cap being composed of two cells. As a rule, however, there is only one pigment-cell in each eye.

In the eye-cell, lying under the pigment-cell, HESSE describes a double row of small rods, lying close to the pigment-cell. This double row of small rods exists, but the two parts of it are not separate, but continuous at both ends, in whatever direction the cell is cut through. So a flat oval body is formed, with a striated wall, lying close to the pigment-cap (fig. 1. *a*), and following in its shape the form of the cap. This body seems to me to be homologous with

¹⁾ Mém. couronn. de l'Acad. roy. de Belgique T. LVI 1898.

²⁾ Wiener med. Wochenschrift 1900.

³⁾ Lehrb. der vergl. Histologie der Tiere 1902.

the "Glaskörper" with a striated wall, as it is found in the eye-cells of the Hirudines. As is the case with those eye-cells, here in *Amphioxus* too the vitreous body seems to be filled with a granular-looking substance (coagulation?) but this was not always clearly to be seen.

Between this body (α), that lies close to the pigmented cap, and the nucleus (fig. 1 k) lying at the other side of the eye-cell, there is in most cases to be seen another beanshaped body, that does not possess a striated wall, but by a clearer tinction with protoplasmic dyes and a more homogeneous substance may be distinguished from the darker and more granular-looking protoplasm of the cell (fig. 1 b).

This body seems to be connected with the perception of light by the eye-cell in the same way as the vitreous body described above. The arrangement of the neurofibrillae in the eye-cells seems to point to this conclusion. Entering the cell at the ventral side of the nucleus, there, where according to HESSE the eye-cell is drawn out to a point, the neurofibril forms a loosely built network round the nucleus. From this network large neurofibrils ascend through the cell and take the beanshaped body (b) between them (fig. 2, fig. 3). Between this body and the pigment-cap these neurofibrils anastomose again and form a second net, which seems to enclose the vitreous body (α) with the striated wall. How the further course of these fibrils is between the vitreous body (α) and the pigment-cap I could not determine with any accuracy.

To obtain good results with the chlorid of gold-method of APÁTHY the sections may not be very much thinner than $10\ \mu$. Now for the study of the eye-cells it is necessary to make sections of about 6 to $7\ \mu$, because in thicker sections the black pigment of the capshaped cell embraces the greater part of the eye-cell and shuts it out from view. It is therefore not possible to get those deep black neurofibrillae, which may be seen so distinctly in the preparations of APÁTHY (the more so as the neurofibrillae of *Amphioxus* are thinner than those of Hirudines); and even in sections of 6 to $7\ \mu$ that part of the neurofibrillae-network, which is lying beneath the pigment-cap is entirely concealed by the pigment-grains. Probably the network is continuous and anastomoses at the other side with the more ventrally lying network.

In what manner the neurofibrillae leave the eye-cell I could see only in a few cases. The fibril seemed then to proceed horizontally for some time but could not be followed any farther.

B. The neurofibrillae in the ganglion-cells.

On the neurofibrillae in the ganglioncells I'll say only a few words.

It would lead us too far to go into details about the arrangement of the neurofibrillae in all the different types of ganglioncells, and besides, that would not be possible without many plates and drawings. I will therefore confine myself here to the following statements:

According to BETHE ¹⁾ in most of the ganglioncells of the vertebrates the neurofibrillae pass through the cellbody without branching or breaking up into a network. Only in the spinal-ganglioncells and in the cells of the lobus electricus of *Torpedo marinatora* BETHE observed networks of the neurofibrillae, and according to this author networks possibly occur in the basal part of the cells of PURKINJE in the cerebellum and in the cells of the cornu Ammonis.

According to BOCHENEK ²⁾ it is on the other hand probable, that in the vertebrate ganglioncells the neurofibrillae form a very fine network with small meshes. The very dense reticulum of neurofibrillae, he was able to demonstrate in the ganglioncells of *HELIX*, forms according to BOCHENEK an intermediate stage between the coarse network in the cells of *Hirudines* and *Lumbricus*, and the very fine network in the vertebrate ganglioncells.

In accordance with the statements by these two authors, we should expect to find in the ganglioncells of *Amphioxus* either a dense reticulum or a mass of disconnected interwoven very fine threads, passing from one process through the cell-body into another process without branching. This is not the case. In most of the ganglioncells the arrangement and distribution of the neurofibrillae in the ganglioncells resembles very much that which is described by APÁTHY in the ganglioncells of *Hirudines* and *Lumbricus*.

Sometimes we find cells as the one shown in fig. 4, where the neurofibrillae pass through the cell-body without interruption, but this is only to be found in a few cases.

In the bigger ganglioncells, which are lying in the dorsal part of the spinal cord and in the dorsal group of ganglioncells behind the brain-ventricle, there is always a network of neurofibrillae branching and anastomosing with each other. After having entered the cell in most cases the neurofibrillae form a network round the nucleus (partially distinguishable in fig. 5). From out this reticulum radial fibrillae go through the cell body to the periphery (often branching on their way) where they form a second network. With this network are connected fibrillae, which pass through one of the processes of the cell (out of the cell or into it?) — in short, a distribution of

¹⁾ Arch. f. Mikrosk. Anatomie, Bd. 55. 1900. P. 513.

²⁾ Le Névraze. Vol. III. Fasc. I, 1901. P. 85.

the neurofibrillae very much like that described by ΑΡΑΤΗΥ in the smaller ganglioncells of *Lumbicus*. The fibrillae however in *Amphioxus* are thinner, and the reticulum finer.

In other ganglioncells there are not two networks (one round the nucleus and one more at the periphery), connected with each other by means of the radial fibrillae, but the neurofibrillae enter the cell, form a network round the nucleus and leave the cell at the other side, without there being any trace of a more peripheral network to be seen.

A connection between different ganglioncells by means of the neurofibrillae, I could not yet state with a sufficient amount of certainty.

In the colossal ganglioncells the "*Kolossalzellen*", lying just in the middle of the spinal cord, the arrangement of the neurofibrillae is very peculiar. From out the colossal nerve-fibres, the axons of these cells, a thick bundle of very thin neurofibrillae, arranged very regularly and equally in the whole axis cylinder, enter the ganglioncell; in the cell-body they pursue their way as a thick bundle that passes round the nucleus, turns upon itself, forms a sort of vortex and then seems to condense itself into a few thick (composed of a great number of elementary fibrillae) fibrillae. Where these fibrils go to, I could not state accurately. In the axons the extremely thin neurofibrillae are closely set and parallel to each other, and so a striking resemblance is formed with the "*sensorische Schläuche*" of *Hirudines* and *Astacus*. During the course of these nerve-fibres through the spinal cord the neurofibrillae are seen to pass one by one every now and then in an oblique direction through the wall of these nerve-fibres; then they are lost in the nervous network without, and could not be followed any farther. Perhaps they are connected there with other ganglioncells, which should be in concordance with the character of the colossal ganglioncells as connecting cells ("*Schaltzellen*").

C. The innervation of the striped muscular tissue.

According to ROIDE¹⁾ the motor nerves simply enter the muscle-plates there where these end, and there is no trace of a motor nerve endplate; according to HEYMANS and VAN DER STRICHT²⁾ however the motor nerves of *Amphioxus* terminate each in a shovelshaped endplate, that lies itself against the muscle-plate just as the motor nerve endplates of the higher vertebrates do. According to their descriptions and drawings the endplates of *Amphioxus* are thick shovel-shaped plates without branchings, without further differentiations (Golgi method).

¹⁾ SCHNEIDER's Zoologische Beiträge. Bd. II, 1888.

²⁾ Mém. couronn. par l'Acad. roy. de Belgique 1898.

Now APÁTHY and RUFFINI¹⁾ were able to demonstrate in homo the existance of "ultraterminal" nerve-fibres, that is to say nerve-fibres which grow out from the branching and thickening of the motor nerve known as "endplate", and enter the muscle-fibre (this could not be made out with absolute certainty) pass through it and in many cases are connected with other endplates. Only a few cases are described but they are sufficient to show that the so-called nerve end-plate is not always to be considered as the real termination of the motor nerves.

The following observations seem to point to the same conclusion.

The thin muscle-plates of *Amphioxus* (fig. 6a) present in longitudinal sections a beautiful cross striation. Each isotropous disc (*i*) is divided into two discs by a delicate, but distinct membrane of KRAUSE; each anisotropous disc (*q*) is composed of two discs, separated by a thin layer, that takes but a faint stain with chloride of gold, the median disc of HENSEN. In the middle of this transparent portion there is sometimes to be seen an extremely delicate line, the membrane of HENSEN.

The membranes of KRAUSE form, as is known, crossnets, which bring the fibrillae of the entire muscle-plate in connection with each other. In the adult animal real muscle-cells are not to be distinguished, there are only the thin flattened muscle-plates to be found, which however in hardened specimens sometime appear to be broken up into rows of flat bundles of fibrillae. This is nothing but an artefact.

In longitudinal sections of *Amphioxus* in which therefore the muscle-plates are cut in the same direction, but mostly appear not as plates but cut obliquely as bundles of muscle-fibres (fig. 6a), there are to be found, in case the sections are coloured after the chloride of gold method, in many places just there where the anisotropous and isotropous discs meet, minute black dots, or small corpuscles; seen under a microscope of the highest magnifying power these dots appear as very delicate cross lines, thickened in the middle, running just between *q* and *i*. In these discs belonging to the same muscle-plate these dots are lying in adjoining discs one just beneath the other, so that rows of black dots running parallel to the myofibrillae are formed. In each muscle-plate such longitudinal rows seem to be distributed with some regularity. These black dots were always found only at one side of the anisotropous disc, and, so it seems, always at the same side of *q*, viz. at that turned caudal. The black dots lying in the same muscle-plate in the same longitudinal row, are often

¹⁾ Rivista di Patologia nervosa e mentale. Vol. V fasc. 10. 1900.

found to be connected with each other by means of very delicate fibrillae, which are running parallel to the myofibrillae. This could be stated in many cases with great clearness. In some cases these fibrillae were straight, in other cases more or less undulating. In fig. 6*a* a longitudinal section through the muscular plates (cut obliquely) is drawn greatly enlarged. The small dots and fibrillae are easily to be seen.

In transverse sections the same rows of fibrillae and black dots were also to be seen, and here they are seen to be distributed more or less regularly on the muscle-plates (fig. 6*b*). At both ends of the black dot here too a delicate black line may be seen, extending for some way along the muscle-plates but then being lost to view. By playing up and down by means of the micrometer screw of the microscope in cross sections too a longitudinal fibril may be made out extending upwards and downwards from the black corpuscle; this fibril is identical with that, which in longitudinal sections was seen to run parallel to the myofibrillae and to connect the black dots of a longitudinal row with each other.

So we find here in the muscle-plates of *Amphioxus* an apparatus, which brings the anisotropic discs of the same muscle-plate in connection with each other, which seems to be distributed with some regularity over the whole muscle-plate, and which gives the staining reaction of the neurofibrillae. Although I could not find the connection of these fibrillae with the motor nerves, still these facts seem to point to the conclusion, that we may regard these fibrillae and their knobshaped thickenings at one side of the anisotropic discs as representing the real innervation-apparatus of the striped muscle-fibres. Sometimes I saw one of the longitudinal fibrillae near the place of attachment of the myofibrillae to the myosepts bend off from the muscle-plate; but it was lost almost immediately between the myofibrillae in the neighbourhood and could not be traced any farther. When we consider however the constant position of the small knobshaped thickenings at one side of the anisotropic disc, the fine often undulated connecting fibrillae, the dark-purple tinction with chloride of gold (Nachvergoldung ΑΡΥΤΗΥ) so characteristic for neurofibrillae, then, I think, it is difficult to avoid the conclusion that they are neurofibrillae.

This seems to me to be important from a general point of view. Although the structure of the striped muscular tissue of *Amphioxus* differs largely from that of the higher Vertebrates, yet the same type of cross striation, that is, the same structure of the myofibrillae, is present in all.

Where now HEYMANS and VAN DER STRICHT found a motor nerve endplate identical with those of the higher Vertebrates and at the side of this structure can be seen an innervation of each anisotropic disc, as I have attempted to show, there is room for the conclusion that in other vertebrates too the so-called motor nerve endplate is not the ending of the motor nerve, but that from here neurofibrillae enter the muscle-fibre, and that every anisotropic disc is innervated. The truth of this surmise, however, must be tested by further study.

Amsterdam, October 1902.

(November 20, 1902).

J. BOEKE. On the structure of the light perceiving cells in the spinal cord, on the neurofibrillae in the ganglioncells and on the innervation of the striped muscles in amphioxus lanceolatus.

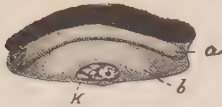


Fig. 1.
Pigment-cup and eye-cell
with vitreous bodies.

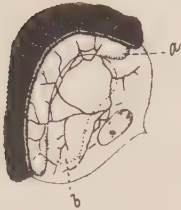


Fig. 2.
Pigment-cup and eye-cell with
the network of neurofibrillae
Enlarg : 800.

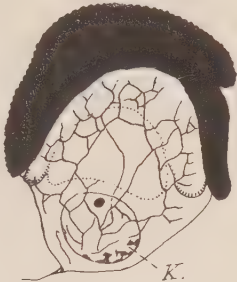


Fig. 3.
Pigment-cup and eye-cell with
network of neurofibrillae.
Enlarg : 1200.



Fig. 4.

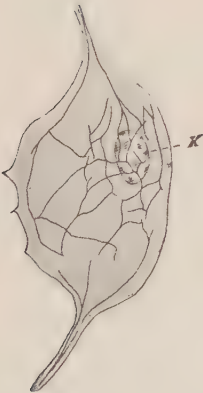


Fig. 5. Arrangement of the neurofibrillae in a
section through a ganglioncell from the dorsal part
of the medulla. Fibrillae drawn with the
drawing apparatus in different optical sections.

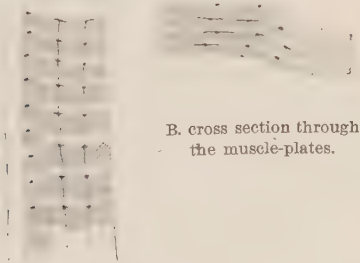


Fig. 6.
A. longitudinal
section.

KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN
TE AMSTERDAM.

PROCEEDINGS OF THE MEETING
of Saturday November 29, 1902.

(Translated from: Verslag van de gewone vergadering der Wis- en Natuurkundige
Afdeeling van Zaterdag 29 November 1902, Dl. XI).

C O N T E N T S.

J. J. BLANKSMA: "The intramolecular rearrangement of atoms in halogen acetanilides and its velocity". II. (Communicated by Prof. C. A. LOBRY DE BRUYN), p. 359.

S. L. VAN OSS: "Five rotations in S_4 in equilibrium". (Communicated by Prof. P. H. SCHOUTE), p. 362.

J. WEEDER: "On interpolation based on a supposed condition of minimum." (Communicated by Prof. H. G. VAN DE SANDE BAKHUYZEN), p. 364.

The following papers were read:

Chemistry. — "*The intramolecular rearrangement of atoms in halogen acetanilides and its velocity*," II. By Dr. J. J. BLANKSMA.
(Communicated by Prof. C. A. LOBRY DE BRUYN).

(Communicated in the meeting of October 25, 1902).

In a former communication¹⁾ it was shown that the conversion of acetylchloranilide in acetic acid solution under the influence of hydrochloric acid proceeds like a monomolecular reaction. In continuing this research the object was to study the influence of:

- 1st. The dilution of the acetic acid with water.
- 2nd. The quantity of added hydrochloric acid.
- 3rd. The solvent (besides acetic acid, alcohols etc.).
- 4th. Different catalysers (HCl , HBr , H_2SO_4).
- 5th. Different groups in the nucleus and their relative positions.
- 6th. The temperature.

First of all the influence of the dilution of the acetic acid was studied, varying proportions of hydrochloric acid being also added. afterwards a few experiments were made in alcoholic solution.

¹⁾ Proc. Royal Acad. Amsterdam. June 29, 1902.

The *modus operandi* was as follows:

A definite quantity (3 to 4 grams) of acetylchloranilide was dissolved in respectively 100, 150, 200 and 250 c.c. of 100 % acetic acid; to this were added 10, 15, 20 or 25 c.c. of 28.67 % hydrochloric acid and the mixture was finally diluted with water to 500 c.c. The experiments were then conducted as described in the previous communication; by applying the formula $k = \frac{1}{t} \ln \frac{A}{A-x}$ the k 's were calculated; t is expressed in minutes.

The following results have been obtained:

in 500 of solution. 10 15 20 25 c.c. hydrochloric acid.

c.c. acetic acid.	100	0.00506	0.00973	0.0189	0.0241
	150	0.00846	0.0186	0.0318	0.0460
	200	0.0157	0.0335	0.0588	
	250	0.0359	0.0719		
	300	0.0836			

in 500 of solution. 10 15 20 c.c. hydrochloric acid.

c.c. alcohol.	200	0.00883	0.0201	0.0341
	250	0.0158	0.0358	0.0591

By means of these figures curves may be constructed either by taking the figures from a horizontal row or those from a column. The first row for instance shows how the velocity of reaction (constant) increases in 20 % acetic acid in the presence of a varying amount of hydrochloric acid (10, 15, 20, 25 c.c.) etc.

In this manner the different series may be represented by the lines *A*, *B*, *C* and *D*.

The first column shows how the velocity of reaction changes with different concentrations of the acetic acid if the amount of the catalyser is constant. These columns are represented by the lines *E*, *F*, *G* and *H*. The alcoholic solution has been represented in the same manner (*A'*, *B'*; *C'*, *D'*, *E'*).

These curves show:

1st. That the velocity of reaction, both in acetic and alcoholic solution, is decreased by addition of water.

2nd. That the velocity of reaction is much accelerated by increasing the catalyser.

3rd. That the curves all end in the origin of the co-ordinates which means that the velocity of change in water without hydrochloric acid is zero so that the substance is stable therein. [Always on condition that light is excluded, (compare first communication)].

On comparing the two tables it will be also noticed that the velocity of reaction is greater in acetic acid than in alcohol; for instance, in a mixture of 200 c.c. of acetic acid and 15 c.c. of hydrochloric acid, $k = 0.0335$; when using 200 c.c. of alcohol and 15 c.c. hydrochloric acid $k = 0.0201$ ¹⁾.

If we compare the curves *E*, *F*, *G* and *H* we notice that on decreasing the concentration of the catalyser, the curves begin to approach the abscissa axis which again shows that, in the absence of hydrochloric acid, the velocity of change in acetic acid or alcohol is zero or in any case very small, which may also be seen from the curves *A*, *B*, *C* and *D*.

A 100 c.c. acet. acid with water to 500 c.c.

B 150 " " " " " " "

C 200 " " " " " " "

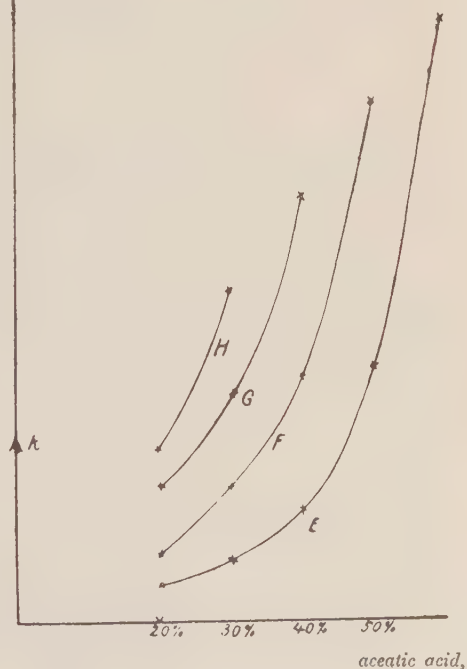
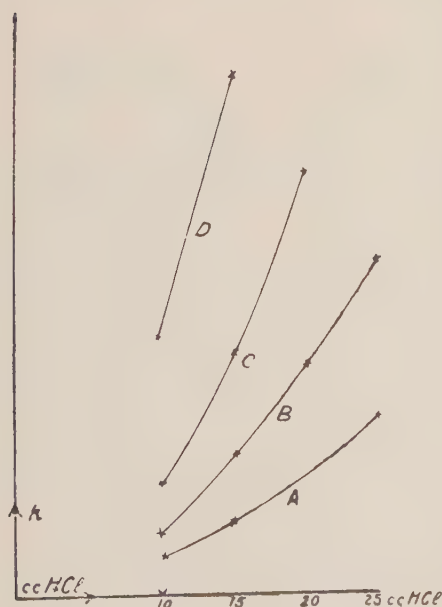
D 250 " " " " " " "

E 10 c.c. HCl in 500 c.c. solution.

F 15 " " " " " "

G 20 " " " " " "

H 25 " " " " " "



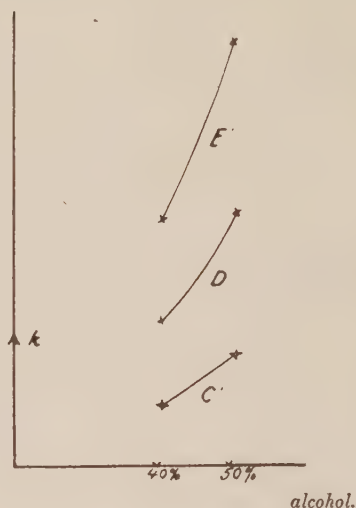
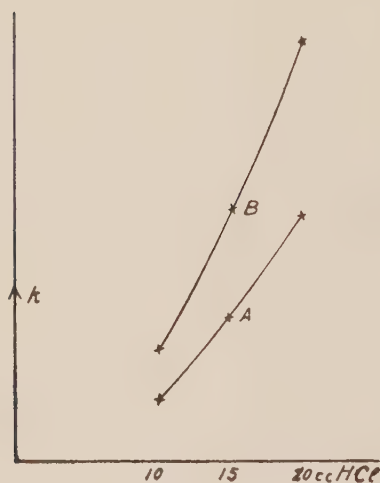
¹⁾ If we calculate number of mols. of alcohol or acetic acid to a given number of mols. of water we see that this difference in velocity of reaction is still greater.

A' 200 c.c. alcohol + water to 500 c.c.
 B' 250 " " + " " 500 "

C' 10 c.c. HCl in 500 c.c. solution.

D' 15 " " " " " "

E' 20 " " " " " "



Mathematics. — "*Five rotations in S_4 in equilibrium.*" By Dr. S. L. VAN OSS, Zaltbommel. (Communicated by Prof. P. H. SCHOUTE).

In a previous paper (these *Proceedings*, Vol. IV, p. 218) the investigation of the elementary motion in S_4 was reduced to the consideration of the elementary motion in S_3 by making use of a principle to be read as follows: A system of rotations about planes *all passing through one and the same point* is in equilibrium when their intersections with an arbitrary S_3 are in equilibrium. Here we mean by section of a rotation with any S_3 the rotation of the intersecting space caused by its component about the plane orthogonally cutting this S_3 in the intersection of the plane of rotation.

As an immediate result of this principle we can state the conditions under which three to seven planes through *one point* can be the planes of a system of rotations in equilibrium. Thus i. a. the condition for four planes, that they must belong to a hyperboloidic pencil, etc. etc.

We now wish to extend this principle in order to arrive by investigation also at the case, that the planes do not pass any longer through one and the same point.

It goes without saying, that if a system of rotations is in equilibrium, its section with every S_3 must be in equilibrium. The question

here, however, is to find out how many of those intersections will have to be examined before we can conclude about the system being in equilibrium or not.

To this end we direct our attention in the first place to the case, that a system Ω has two sections in equilibrium, namely with the spaces A and B .

If the section Ω/A is in equilibrium, then Ω must necessarily be reducible to a single rotation about a plane in A ; likewise, if Ω/B is in equilibrium, then Ω can be reduced to a single rotation about a plane in the space B .

So from the equilibrium of the sections it does not yet follow that the system itself is in equilibrium, for the possibility remains that it may be reducible to a rotation about the plane common to the two spaces of intersection.

If, however, we can point out three spaces S_3 not passing through the same point, their sections being in equilibrium, then the equilibrium of the system itself is guaranteed. Let us now apply this result to determine five planes which can be the bearers of a system of rotations in equilibrium.

The necessary condition which these planes must satisfy is that they be intersected by three spaces S_3 , not passing through one and the same point, in rays of a linear congruence. In other words: They must intersect three pairs of straight lines, the director lines of these congruences.

Now we know that in S_4 there are just 5 planes intersecting 6 given lines. They are the five "associated planes" of SEGREG (Rend. di circ. math. di Palermo, t. II, 1888).

Now we have the necessary condition; we shall show, that it is also sufficient.

Let Ω be a system of rotations about 5 associated planes, A an S_3 so that Ω/A is in equilibrium. If Ω were not in equilibrium itself, this system would have to be equivalent to a rotation ω about a plane α in A . If we reverse the direction of the rotation about this plane, then the combination $(\Omega - \omega)$ is in equilibrium. If we now consider a second intersecting space B , not through α , then the planes of Ω are intersected in 5 rays of a congruence and the plane of ω in a line not belonging to this congruence. The section of B with the combined system $\Omega - \omega$ would, however, have to be in equilibrium. This is impossible, unless ω is equal to naught, i. e. unless Ω is in equilibrium.

Nothing remains but to determine the ratios of the intensities of the rotations of Ω . This should be done as follows:

We consider an arbitrary S_3 which intersects the planes of Ω in the axes of rotation of the section; the determination of the ratios of the intensities belonging to them is a well known problem.

If, finally, we notice that between the intensities ω and ω' of a rotation in S_4 and its intersection with a space A the relation $\omega' = \omega \sin(A\omega)$ exists, then in this way the intensities of the rotations about the five associated planes have become known quantities.

Mathematics. — "*On interpolation based on a supposed condition of minimum.*" By J. WEEDER. (Communicated by Prof. H. G. VAN DE SANDE BAKHUYZEN.)

For the reduction of the daily rates of the standard clock in the Leyden Observatory I have developed a method of interpolation, which may perhaps also be profitably used for other investigations.

The following is the problem we have to deal with: a variable quantity, here the correction of the clock, is given for a series of instants, during a long period, with unequal intervals; how can we find an intermediate value of that correction at any moment.

First I tried to solve this problem with the limiting condition that for all the intervals of time which enter into the calculation there is a smallest common divisor, which we take as unit of time.

1. Let S (clock correction) be the variable quantity, and g (rate) the amount by which it increases during a unit of time. Let S_p and S_q , be two successively determined values of S separated by m units of time, then $\frac{S_q - S_p}{m}$ is the average increase per unit; that increase

is represented by Q_m . Hence the m quantities $g_1 g_2 \dots g_i \dots g_m$ of the interval considered depend on the relation $\sum_{i=1}^{i=m} g_i = S_q - S_p = m Q_m$ and a similar relation exists for each interval between two consecutive determinations of S .

In order to determine the quantities g , I put the condition that the sum of the squares of the differences of the first order for the whole period of observation should be a minimum. This condition of minimum was selected with a view to the special case where we have to interpolate between the clock corrections, but I doubt whether in all cases these interpolated values will be the most probable ones. Leaving aside for the moment these considerations, I go on developing the problem in hand. The quantities which correspond to an interval of m units occur only in the following terms

and taking their sum; in the resulting equation all unknown quantities $g_1 \dots g_m$ except g_i are eliminated. That equation got by summation is:

$$-g_p(m-i+1) + (m+1)g_i - i g_q + \frac{1}{2} i (m-i+1) (m+1) k_m = 0$$

which yields:

$$g_i = \frac{m-i+1}{m+1} g_p + \frac{i}{m+1} g_q - \frac{i(m-i+1)}{2} k_m$$

hence
$$g_1 = \frac{m}{m+1} g_p + \frac{1}{m+1} g_q - \frac{1}{2} m k_m$$

and
$$g_m = \frac{1}{m+1} g_p + \frac{m}{m+1} g_q - \frac{1}{2} m k_m.$$

The quantities g_p and g_q are still unknown and depend on the quantities Q of the neighbouring intervals; they may be derived from them by means of successive approximation.

It gives some advantage to determine $\frac{1}{2}(g_p+g_1)$ and $\frac{1}{2}(g_m+g_q)$ by approximations, because then we shall have to approximate only one quantity for each S . The approximation may be made in the following way: we put $\frac{1}{2}(g_p+g_1)=c_p$ and $\frac{1}{2}(g_m+g_q)=c_q$, then we obtain:

$$k_m = \frac{6}{m^2+2} (c_p + c_q - 2 Q_m)$$

$$g_p = -\frac{3m}{m^2+2} Q_m + \left(1 + \frac{2m^2+1}{m(m^2+2)}\right) c_p + \frac{m^2-1}{m(m^2+2)} c_q$$

$$g_q = -\frac{3m}{m^2+2} Q_m + \frac{m^2-1}{m(m^2+2)} c_p + \left(1 + \frac{2m^2+1}{m(m^2+2)}\right) c_q.$$

For the next interval of n units of time between the determinations S_q and S_r we have the following equation:

$$g_m = -\frac{3n}{n^2+2} Q_n + \left(1 + \frac{2n^2+1}{n(n^2+2)}\right) c_q + \frac{n^2-1}{n(n^2+2)} c_r.$$

As $g_q + g_m = 2 c_q$ we obtain when finding the summation of the two last equations a recurrent equation containing 3 consecutive quantities c , so that c_q can be expressed in c_p and c_r . This equation can also be written thus:

$$\left\{ \frac{2m^2+1}{m(m^2+2)} + \frac{2n^2+1}{n(n^2+2)} \right\} c_q = -\frac{m^2-1}{m(m^2+2)} c_p + \frac{3m}{m^2+2} Q_m + \\ + \frac{3n}{n^2+2} Q_n - \frac{n^2-1}{n(n^2+2)} c_r. \quad \dots \dots \dots (B)$$

For the first interval considered here the first of the equations (A) is $g_1 - g_2 + k_m = 0$. This equation may also be written in the general form by putting $-g_1 + 2g_1 - g_2 + k_m = 0$, thus assuming that the value of g preceding g_1 and c belonging to the first observation are both equal to g_1 . In the same way c belonging to the last observation is equal to the last g of the last interval. Between each three consecutive quantities c , therefore, a relation exists of the form (B) and two other equations are added to the beginning and to the end of this series, each containing only two values c derived from the formulae for g_p and g_q . Let c_a and c_b be the first two and c_y and c_z the last two quantities c , then we obtain by substituting c_a for $g_p = c_p$ and c_b for c_q the first condition, and by substituting c_z for $g_q = c_q$ and c_y for c_p the last condition of the series which determine the values c .

If the lengths of the limiting intervals are represented by μ and ν these equations are:

$$(2\mu^2+1) c_a = + 3\mu^2 Q_\mu - (\mu^2-1) c_b \\ (2\nu^2+1) c_z = + 3\nu^2 Q_\nu - (\nu^2-1) c_y$$

The series (B) and these two equations determine all the quantities c . If we solve them by approximation our purpose is soon gained; we assume to the first approximation $c_q = \frac{nQ_m + mQ_n}{m+n}$ and c_a and c_z equal to the values of Q of the first and the last interval respectively. From the equations (B) we derive the first corrections $\Delta_1 c_p$, $\Delta_1 c_q$, etc. and $\Delta_2 c_q$ is derived from the formula:

$$\left\{ \frac{2m^2+1}{m(m^2+2)} + \frac{2n^2+1}{n(n^2+2)} \right\} \Delta_2 c_q = -\frac{m^2-1}{m(m^2+2)} \Delta_1 c_p - \frac{n^2-1}{n(n^2+2)} \Delta_1 c_r.$$

In this interpolation we determine g_i and S_i of an interval of m units according to the formulae:

$$g_i = \left(\frac{1}{4} m k_m + c_p + \frac{c_p - c_q}{2m} \right) i - \left(\frac{m+1}{2} k_m + \frac{c_p - c_q}{m} \right) i^2 + \frac{1}{2} k_m i^3 \\ S_i = S_p + \left(c_p - \frac{1}{6} k_m \right) i - \left(\frac{m}{4} k_m + \frac{c_p - c_q}{2m} \right) i^2 + \frac{1}{6} k_m i^3.$$

2. In the previous section the observed and the interpolated quantities S , occurring in the problem discussed, form a series of

discrete values corresponding to an arithmetical series of the argument; now I will remove the restriction of commensurable arguments and will make this mode of interpolation applicable to a continuous varying quantity and an arbitrary argument by putting for the ratio of that series the infinitely small value dt . The condition

of minimum then becomes $\int_a^z \left(\frac{d^2 S}{dt^2} \right)^2 dt = \min.$

The formulae for this continuous interpolation may be derived independently, but it is shorter to derive them from the corresponding formulae of the discrete interpolation developed above. For the present I shall put for the lengths of the intervals between which we have to interpolate m' and n' , for the derived values $\frac{dS}{dt}$ of the interpolated function g' , to distinguish them from the letters we have used in the former problem.

Instead of m and n we have $\frac{m'}{dt}$ and $\frac{n'}{dt}$; for c_p, c_q, c_r we must substitute the quantities $g'_p dt, g'_q dt, g'_r dt$, and for Q_m and Q_n the quantities $\frac{S_q - S_p}{m'} dt$ and $\frac{S_r - S_q}{n'} dt$ or $Q_{m'} dt$ and $Q_{n'} dt$.

After dividing the relations (B) by dt^2 and omitting the infinitely small values we have:

$$\left(\frac{2}{m'} + \frac{2}{n'} \right) g'_q = -\frac{1}{m'} g'_p + \frac{3}{m'} Q_{m'} + \frac{3}{n'} Q_{n'} - \frac{1}{n'} g'_r$$

from which, after dropping the accents, we get:

$$g_q = \frac{nQ_m + mQ_n}{m+n} + \frac{n(Q_m - g_p)}{2(m+n)} + \frac{m(Q_n - g_r)}{2(m+n)} \quad \dots \quad (C)$$

to which we must add as first and last equations:

$$g_a = Q_\mu + \frac{Q_\mu - g_b}{2} \quad \text{and} \quad g_z = Q_\nu + \frac{Q_\nu - g_y}{2}$$

For k_m we substitute $\frac{6}{m'^2} (g'_p + g'_q - 2 Q_{m'}) (dt)^3$; for i we substitute $\frac{t}{dt}$, if t represents the time between the last preceding observation at the moment for which we interpolate. These substitutions in the formula for S_i yield a formula for S_t , which, after the omission of infinitely small values and accents, is:

$$S_t = S_p + g_p t - \left[\frac{3}{2m} (g_p + g_q - 2Q_m) + \frac{g_p - g_q}{2m} \right] t^2 + \frac{g_p + g_q - 2Q_m}{m^2} t^3$$

By substituting in the above formula $m-t'$ for t , we obtain for S_t a formula developed according to the ascending powers of t' , the interval between the moment for which we interpolate and the moment of the next observation. It is simpler to find the same formula by imagining the interpolation to be made in the inverse direction, so that the quantities g and Q change signs and the indices p and q change places. Hence :

$$S_{m-t'} = S_t = S_q - g_q t' + \left[\frac{3}{2m} (g_p + g_q - 2Q_m) - \frac{g_p - g_q}{2m} \right] t'^2 - \frac{g_p + g_q - 2Q_m}{m^2} t'^3.$$

For S_t to be interpolated in the following interval we use :

$$S_t = S_q + g_q t - \left[\frac{3}{2n} (g_q + g_r - 2Q_n) + \frac{g_q - g_r}{2n} \right] t^2 + \frac{g_q + g_r - 2Q_n}{n^2} t^3.$$

Therefore the formulae on either side of each observation are different. If in the latter formula t is negative and $-t'$ is substituted for it, the resulting formula differs from the preceding one only in the coefficients of the terms of the 3rd degree. The coefficients of the terms of the 2nd degree have become equal by satisfying the relation (C).

Therefore we also obtain the interpolated function if, by starting from a value (S_q) derived from observation, we represent the values of S_{-t} and S_{+t} for the moments between that observation and the next preceding one and those between that observation and the next following one by the formulae :

$$S_{-t} = S_q - g_q t + c_q t^2 - e_m t^3 \quad \text{and} \quad S_{+t} = S_q + g_q t + c_q t^2 + e_n t^3.$$

Taking this as basis, we find :

$$c_q = \frac{+g_p - 3Q_m + 2g_q}{m} = \frac{-2g_q + 3Q_n - g_r}{n} \quad e_m = \frac{g_p + g_q - 2Q_m}{m^2} \quad e_n = \frac{g_q + g_r - 2Q_n}{n^2}$$

The integral $\int_a^z \left(\frac{d^2 S}{dt^2} \right)^2 dt$, which becomes a minimum through this

interpolation, is equal to the sum of the integrals between two consecutive observations, and each of these integrals can be expressed in the coefficients of the interval in the following manner :

$$I_n = \int_q^r \left(\frac{d^2 S}{dt^2} \right)^2 dt = \frac{3(g_q + g_r - 2Q_n)^2}{n} + \frac{(g_q - g_r)^2}{n} = 3n^3 e_n^2 + \frac{(g_q - g_r)^2}{n}$$

or :

$$I_n = \frac{4}{3} n (c_q^2 + c_q c_r + c_r^2).$$

For the total integral ΣI_n we can also derive a simple form by integrating partially:

$$\int_a^z \left(\frac{d^2 S}{dt^2} \right)^2 dt = \left[\frac{dS}{dt} \frac{d^2 S}{dt^2} \right]_a^z - \int_a^z \frac{dS}{dt} \frac{d^3 S}{dt^3} dt.$$

For the first moment a and the last moment z , $\frac{d^2 S}{dt^2} = 0$, as follows from the first and the last equations belonging to (C). For each interval between two observations $\frac{d^3 S}{dt^3}$ is a constant quantity. Hence we find:

$$I = \Sigma 6 e_n (S_q - S_r)$$

where the summation extends over all the intervals between the observations. We can easily find a simple expression for the differential quotient of I according to each of the observed values, which may be useful when we want not only to interpolate for an intermediate moment but when at the same time we have to determine the most probable values of the observed quantities. For then the difficulty presents itself how to find the best method for diminishing the amount of the minimum value I by applying corrections to the observations, of which corrections the mean value is known.

In doing so heed must be taken that these corrections, being errors of observation, shall satisfy the law which determines their probabilities as functions of their magnitudes.

I have not yet reached a satisfactory solution of this problem. The following remarks, however, on this subject seemed important enough to be communicated.

3. Let L_p, L_q, L_r be the observed quantities, free from errors of observation, and f_p, f_q, f_r the errors themselves.

If we have developed the interpolation by means of the quantities L and f separately, we obtain the formulae:

$$\begin{aligned} L_t &= L_q + G_q t + C_q t^2 + E_n t^3 \\ f_t &= f_q + \beta_q t + \gamma_q t^2 + \epsilon_n t^3. \end{aligned}$$

By means of the summation of these two formulae we get:

$$S_t = S_q + g_q t + c_q t^2 + e_n t^3.$$

If we apply a partial integration to $\int_a^z \frac{d^2 L}{dt^2} \cdot \frac{d^2 f}{dt^2} dt$, we get:

$$\left[\frac{d^2 L}{dt^2} \frac{df}{dt} \right]_a^z - \int_a^z \frac{d^3 L}{dt^3} \frac{df}{dt} dt$$

or

$$\left[\frac{dL}{dt} \frac{d^2 f}{dt^2} \right]_a^z - \int_a^z \frac{dL}{dt} \frac{d^3 f}{dt^3} dt$$

In either case the integrated parts are equal to 0, because at the beginning and end $\frac{d^2 L}{dt^2}$ and $\frac{d^2 f}{dt^2}$ are zero.

In this way we find the relation:

$$\sum E_n (f_q - f_r) = \sum \epsilon_n (L_q - L_r).$$

In the same way we find the relation:

$$\sum e_n (f_q - f_r) = \sum \epsilon_n (S_q - S_r).$$

By applying the corrections $-f$, the minimum I_S becomes the minimum $I_L = I_S - f$.

$$\begin{aligned} I_S - f &= \sum 6 (e_n - \epsilon_n) (S_q - f_q - S_r + f_r) = \\ &= \sum 6 e_n (S_q - S_r) - \sum 6 \epsilon_n (S_q - S_r) - \sum 6 e_n (f_q - f_r) + \sum 6 \epsilon_n (f_q - f_r) \end{aligned}$$

which expression by means of the latter relation may be reduced to:

$$I_S - f = I_S - 12 \sum e_n (f_q - f_r) + \sum 6 \epsilon_n (f_q - f_r).$$

For infinitely small values f , the last term in the expression given above becomes of the order f^2 so that we find $\frac{\partial I_S}{\partial S_q} = 12(e_n - e_m)$.

This result enables us to determine the set of small corrections, which, when applied to the quantities S , diminish I_S by the greatest amount. These corrections will be proportional to the abrupt changes of $\frac{d^3 S}{dt^3}$.

The variations in the interpolation coefficients g , c , e , resulting from these corrections are found by repeating the interpolation, with this sole difference that for the observed quantities S we substitute the abrupt changes of $\frac{d^3 S}{dt^3}$.

As a rule a set of corrections of this kind will not show the character of the errors of observation and therefore be dissimilar to the set of errors which actually exist in the observed quantities S . We may also determine a limit which should not be passed in the rectification.

If the quantities f represent the real errors, we have:

$$I_S = I_L + \sum 12 E_n (f_q - f_r) + \sum 6 \epsilon_n (f_q - f_r)$$

The coefficients E of the interpolation formula between the correct quantities S and the errors f being as a rule entirely independent, we must assume that in $\sum 12 E_n (f_q - f_r)$ the positive

and negative terms neutralize each other for the greater part. Hence the difference $I_S - I_L$ does not exceed $\Sigma 6 \varepsilon_n (f_q - f_r)$, the value of which depends only on the errors and the lengths of the intervals; the mean value of this expression for every possible distribution of the errors of the observations may be derived from the mean error of those observations.

This is the utmost limit to which by means of corrections to the observed quantities S we can diminish I_S , lest the interpolation curve found should assume a less sinuous form than would be probable with regard to the results of the observations and their precision.

Here follows an example of the computation.

The annexed table contains the interpolation coefficients of a part (period 1882 June 8 to August 30), taken from a longer series of observed rates of the clock Hohwü 17. Therefore the coefficients at the limits of this period are not in accordance with the boundary-conditions supplying the formula (C).

We compute the interpolated clock corrections by means of the formula:

$$S_t = S_q + t \left(g_q + n c_q \frac{t}{n} + n^2 e_n \frac{t^2}{n^2} \right)$$

S_q is the clock correction of the last preceding observation and the coefficients g_q , nc_q , $n^2 e_n$ are given in the columns 5, 6 and 7; they are expressed in the unit 0.001. The values g_q and nc_q to be used are placed a little above the horizontal line corresponding to the length of the interval expressed in days, which interval contains the moment t for which we interpolate. Because of its connection with the constant derivative of the third order of the interpolation curve within each interval, the coefficient $n^2 e_n$ for each interval has been placed on the horizontal line of that interval.

The 8th column contains the coefficients e and the 9th their differences σ by passing from one interval to the other. For each of these differences I have calculated the variation $\Delta\sigma_q$ of a given σ_q , as the corresponding correction of the clock S_q increases by ± 0.100 while the other corrections remain unmodified; they are given in the 10th column. By the increase $\Delta S_q = - \frac{\sigma_q}{\Delta\sigma_q} \times 0.100$ the difference σ_q becomes zero, so that by means of this increase we obtain the same result as if in the determination of the interpolation curve we had omitted the observation S_q . Hence the correction of the clock S_q derived from this interpolation is equal to the observed

Duration of the intervals in days $m, n.$	Mean daily rates $Q.$	$\frac{mQ_m + nQ_n}{m+n}$	Correction term $\frac{m(Q_m - g_f) + n(Q_n - g_f)}{2(m+n)}$	g_f coefficient of t .	$n.c.$ coefficient of β .	$n^2c.$ coefficient of β .	$c.$	$\sigma = \epsilon_n - \epsilon_m$	$\Delta \sigma$ for a variation $\Delta S = + 0s.100.$	Obs. - Comp. = $\frac{\sigma}{\Delta \sigma} \times 0s.100.$
4	135	118	-03	115	+ 63	- 43	- 2 7	- 7.0	+ 5.4	-0.13
4	086	110	+02	112	- 62	+36	+ 2.2	+ 4.9	+ 4.0	+0.12
4	126	106	-10	096	+ 44	-14	- 0.9	- 3.1	+ 3.9	-0.08
4	126	126	+16	142	+ 04	-20	- 1.2	- 0.3	+ 3.7	-0.01
5	073	102	-12	090	- 68	+51	+ 2.0	+ 3.2	+ 3.0	+0.11
3	129	108	- 01	107	+ 52	-30	- 3.3	- 5.3	+ 4.1	-0.13
7	104	122	-01	121	- 94	+77	+ 1.6	+ 4 9	+ 3.3	+0.15
1	163	156	+08	164	+ 18	-19	-19.	-20 6	+ 26.0	-0.08
4	064	143	00	143	-150	+71	+ 4.4	+23.4	+ 29.3	+0.08
3	094	081	-25	056	+ 46	-08	- 0.9	- 5.3	+ 6.5	-0.08
4	132	110	+14	124	+ 32	-24	- 1.5	- 0.6	+ 5.6	-0.01
5	090	113	+03	116	- 50	+24	+ 1.0	+ 2.5	+ 3.0	+0.08
3	089	089	-01	088	+ 14	-13	- 1.4	- 2 4	+ 4.2	-0.06
5	070	082	-05	077	- 45	+38	+ 1.5	+ 2 9	+ 4.3	+0.07
3	110	095	+06	101	+ 43	-34	- 3.8	- 5.3	+ 4.6	-0.12
4	070	093	-08	086	- 78	+63	+ 3.9	+ 7.7	+ 6.4	+0.12
1	124	113	+05	118	+ 28	-22	-22.	-25.9	+ 57.0	-0.05
1	087	106	+02	108	- 38	+17	+17.	+39.	+167.	+0.02
2	097	090	-07	083	+ 31	-17	- 4.2	-21.2	+ 85.0	-0.03
3	107	101	-07	094	- 28	+41	+ 4.6	+ 8.8	+ 21.9	+0.04
1	160	153	+08	161	+ 33	-25	-25.	-29.6	+ 57.8	-0.05
2	105	148	+04	152	- 84	+37	+ 9.2	+34.2	+114.	+0.03
6	110	106	-11	095	+ 81	-66	- 1.8	-41.0	+ 10.6	-0.10
4	016	054	+05	059	- 77	+34	+ 2.1	+ 3.9	+ 2.6	+0.15
		021	-14	007	+ 25			- 2.5	+ 3.8	-0.07

S_q diminished by $\frac{\sigma_q}{\Delta\sigma_q} \times 0^s.100$. These differences Obs.—Comp. given in seconds of time, are contained in the 11th column.

From the developed formulae I derived for these 24 intervals the value $I_S = \sum \frac{4}{3} n (c_q^3 + c_q c_r + c_r^2) = 69500$, while for all the different manners of distribution of the errors of observation the mean of all the values $I_f = \sum 6 \epsilon_n (f_q - f_r)$, which values depend only on the magnitude of the errors and on their distribution is equal to 30500. In the computation the mean error of the observations has been put 0^s.028, which value must be regarded as the smallest that can be assumed on the strength of other investigations. Therefore the sinuosity of the interpolation curve must be ascribed for a great part to errors of observation.

KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN
TE AMSTERDAM.

PROCEEDINGS OF THE MEETING
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The following papers were read:

Chemistry. — "*Tin amalgams*". By Prof. H. W. BAKHUIS ROOZEBOOM.

(Communicated in the meeting of November 29, 1902).

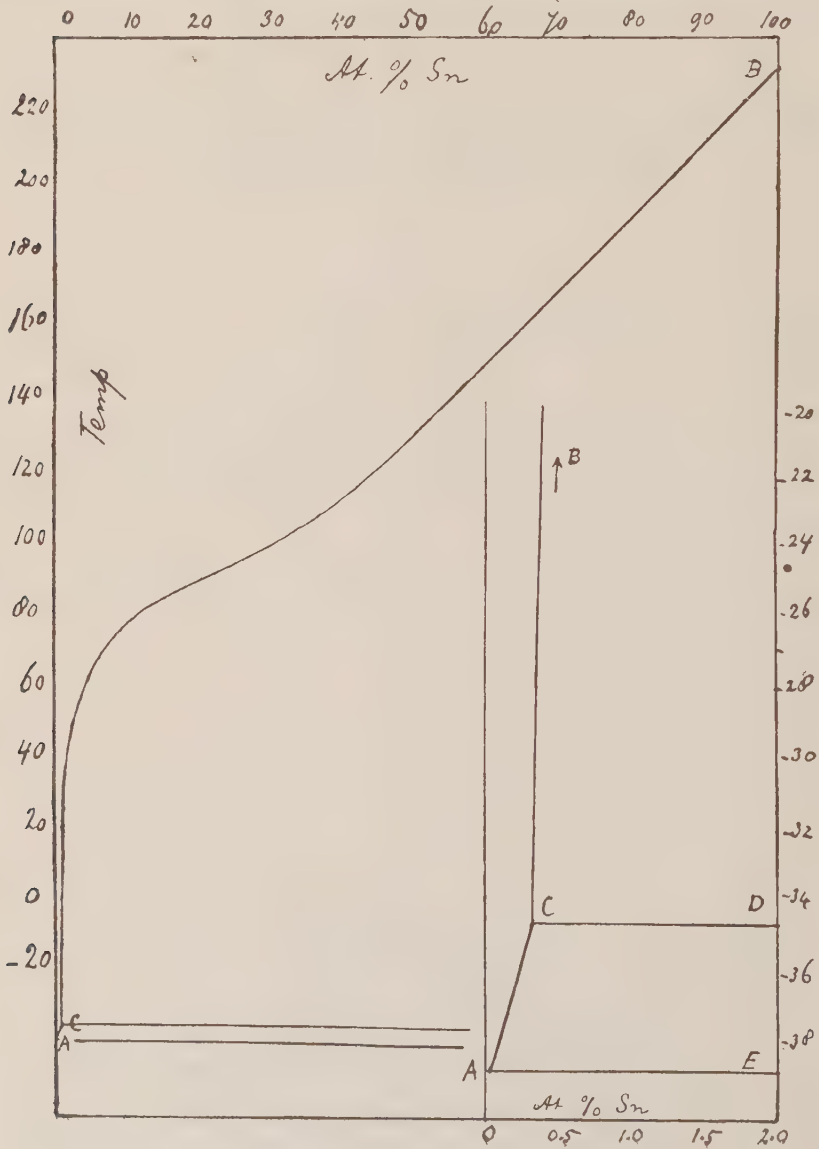
As the number of properly studied amalgams is still very small
I directed Dr. VAN HETEREN to conduct an investigation on tin
amalgams in connection with the research on cadmium amalgams
by Dr. BIJL. The more important results are communicated here.

In the liquid condition tin and mercury are miscible in all pro-
portions. From the different mixtures a solid phase is deposited at
different temperatures. The points at which solidification begins are
indicated in the accompanying figure by two lines *AC* and *CB*

which meet each other at C (0.3 at. % Sn and $-34^{\circ}.5$) in a sharp angle.

As the line CB ends in the melting point of tin, the solid phase which deposits on cooling must be either tin or mixed crystals in which ordinary tin occurs as a component. On analysis, the solid phase which has separated from the liquid amalgam at 25° was found to be composed of 94 atom % Sn.

On account of the difficulty of obtaining trustworthy results in.



LINE BC.

At. % Sn.	Temp.	At. % Sn.	Temp.
100	231°.6	20.37	90°.0
89.95	211 .6	10.79	79 .7
76.62	183 .7	5.17	65 .2
61.44	155 .2	1.20	25 .0
49.99	133 .4	0.60	0 .0
35.33	107 .4	0.36	—18.8
28.96	99 .0	0.30	—34.5

this manner, measurements of the *E. M. F.* were also made at 25° of amalgams of 0.001—100 atom % Sn against an amalgam of 16 atom %.

These measurements led to the results that the unsaturated amalgams have a *E. M. F.* rising with the amount of tin until at 1.2 atom % saturation sets in. From this concentration up to 99 atom % the potential remains unchanged, consequently two phases of unchangeable concentration must exist between these limits; one of these is the liquid one of 1.2 %, the other the solid one containing 99 atom %.

At 25° the crystals deposited therefore consist of nearly pure tin which is the case in a still greater degree at higher temperatures. By a comparison of the values of the *E. M. F.* for amalgams of which the whole mass was liquid at 25° and 50° the heat of amalgamation could be calculated. The introduction of 1 gram-atom of Sn into a liquid amalgam with 0.01—1.00 atom % Sn, therefore nearly pure Hg, absorbs about 3000 calories.

The line *CB* may also be considered as the line of the solutions saturated with Sn. It takes a very peculiar course. The part from 120° up to the melting point of tin is nearly straight, the centre part shows a very rapid increase of the solubility with the temperature, the lower part, however, an exceedingly small increase and also an exceedingly small solubility so that the line approaches very closely the Hg-axis. In the lower part of the figure (p. 374) this part with its course towards the melting point of Hg has been drawn on a larger scale.

The extraordinarily great curvature of the central part of the line would lead to the supposition that the liquid mixtures of $\text{Sn} + \text{Hg}$ in the absence of a solid phase would on further cooling separate into two layers.

On cooling below -34.5° a change takes place in all amalgams from 0.3 to 85 %, accompanied by a decided evolution of heat and decrease of volume. With increasing concentrations of Sn it first increases but then decreases in intensity. The maximum lies near 50 %. This change occurs in the figure on the line CD which therefore runs to at least 85 %.

The change causes a new phase to appear which also belongs to the second solidifying-line CA . The maximum in the intensity of the change on CD at about 50 % would lead us to suppose that mixed crystals having about this composition are formed. The modification of tin therein contained must differ from ordinary tin.

Between -34.5 and -38.5 these mixed crystals continue to be deposited from the mother-liquor (which moves along the line CA), this is accompanied by expansion. This change in volume diminishes as the amount of tin present increases and dies out near 75 %. The solidification point of pure mercury and also the final solidification point of all amalgams containing up to about 60 % Sn, lies at -38.6 (line AE). As the line CA of the saturated solutions also ends here it would seem that at the solidifying point of Hg, the solubility of tin has decreased to 0, so that instead of a eutectic mixture only the remaining mercury solidifies.

Still, the point A bears quite the characteristic of a eutectic point as not only the line AE is horizontal, but all mixtures up to 60 % Sn also remain a shorter or longer time at this temperature which proves that a residual liquid is solidifying completely.

A great uncertainty still exists as to the nature of the tin-modification which occurs in mixed crystals below -34.5 chiefly because it has so far not been possible to discover the part played in the amalgams by the grey modification of tin which may occur below 20°C .

But from the change in volume which takes place in the different transformations at and below -34.5 we may argue that the specific volume of the tin must be smaller than that of the grey modification and larger than that of liquid and, therefore, also of ordinary tin.

Chemistry. — "*Benzidine transformation.*" By Dr. J. POTTER VAN LOON (Groningen). (Communicated by Prof. C. A. LOBRY DE BRUYN).

(Communicated in the meeting of November 29, 1902).

It is known that hydrazobenzene when treated with a dilute mineral acid is converted into benzidine and diphenylene, benzidine being, however, the main product. I endeavoured to ascertain the proportion in which the isomers are formed and in how far this depends on the temperature and the concentration of the acid and I further attempted to measure the velocity with which the transformation takes place under definite circumstances.

Benzidine was obtained pure by recrystallisation from water and distillation in vacuo; the melting point of this substance was 128° which is in agreement with the statements of MERZ and STRASSER. (Journ. f. Pract. Ch. N. F. 60. 186).

For the preparation of hydrazobenzene, azobenzene was used as the starting point: this was purified by distillation and then reduced with zinc dust in an alcoholic alkaline solution. The hydrazobenzene so obtained was dissolved by warming in alcohol and the still yellow liquid decolorised by means of ammonia and zinc dust: the filtrate deposited pure white crystals of hydrazobenzene which could be separated unaltered from the liquid. A determination of the melting point gave as result 122° .

For the study of the transformation it was necessary to have a method for the quantitative determination of benzidine. It was found possible to do this gravimetrically by adding potassium sulphate to a solution containing not too much free acid and so precipitating the base as sulphate which was then collected on a weighed filter. According to my experiments, the slight solubility of benzidine sulphate amounts to 5—6 milligrams per 100 cc. of water at the ordinary temperature and consequently a correction should be applied. To ascertain in what proportion the two bases are formed during the transformation of hydrazobenzene, weighed quantities of this substance were put into bottles of about 120 cc. capacity and then shaken with a definite solution of an acid until all had dissolved. The benzidine present in the solution was then estimated, as directed, and the proportion calculated from the two data.

At the ordinary temperature, $N/10$ hydrochloric acid used in this manner causes 84 per cent of the hydrazobenzene to be converted into benzidine. Normal hydrochloric, hydrobromic acids convert 90

per cent of the same into benzidine. At a higher temperature the proportion is another, for in four experiments with one-tenth normal hydrochloric acid; nitric acid, sulphuric acid and hydrobromic acid the proportions at a 100° were respectively 66.4, 67.3, 63.1 and 65.8 per cent, therefore, much lower.

To get some data respecting the velocity of reaction a beaker with 50 per cent alcohol which contained hydrochloric acid in tenth-normal concentration was put into a thermostat and while stirring violently and passing a current of carbon dioxide over the surface a few grams of hydrazobenzene were introduced into the liquid in which that substance is but little soluble.

At 25°, the velocity appeared to be dependent on the concentration of the acid and it increased more rapidly than the concentration. The experiments are being continued in the two directions indicated above.

(Chem. Lab. Univers. *Groningen*).

Physiology. — "*On the duration of the compensatory pause after stimulation of the auricle of the mammalian heart.*" By Prof. K. F. WENCKEBACH. (Communicated by Prof. PEKELHARING).

(Communicated in the meeting of 29 November 1902).

When an extra-systole is set up by artificial stimulation of the ventricle or auricle of the beating frog's heart, this extra-systole is followed up by a pause longer than the pause succeeding a spontaneous systole. This long interval was studied by MAREY, DASTRE and others, and called a compensatory pause, because the longer quiescence of the heart was regarded as a compensation for the extra activity of the heart muscle. And it was not without reason that the word "compensation" was used, because the pause after an extra-systole is of such length, that the following spontaneous contraction just commences in the moment when it would have set in if, instead of an extra, a spontaneous systole had preceded. ENGELMANN (6) has given a simple and exhaustive explanation of the pause: the normal, physiological stimulus to contraction reaching the heart from the vena cava and causing it to contract finds, after an extra-systole auricle and ventricle in a refractory phase and so it cannot cause a contraction. It is only the following stimulus which finds the heart again in a condition in which it can react on that stimulus; the contraction (the "post compensatory") then commencing, presents

outside to the vena cava, but that it originates in that place in a definite period. It is certainly the most natural and the most suitable explanation of the phenomenon to assume that at the venae cavae (as is known to be the case in less degree in the other parts of the heart) continually stimulating matter is formed, till this obtains such a strength that a contraction is caused. When however, the muscle fibres contract the stimulating matter seems to have been used up or at least to have been destroyed, so that every time after a contraction the same time is wanted to produce new stimulating matter to such a strength that again a contraction follows. This destroying of the stimulating matter (dissociation in Ions, chemical changes or whatever this may be) always takes place when there is a contraction, whether the systole is caused by the stimulating matter itself or caused by a stimulus induced from elsewhere. For it is a well-known fact, that by artificial stimulation of the auricle or the ventricle, more frequent than the spontaneous rhythm, the latter can be entirely overpowered.

Another explanation is that at the vena cava there is a continual stimulation constant in strength, expressing itself periodically in systoles, because with each systole irritability, contractility and conductive power of the heart muscle are neutralized; so if a systole has taken place it always again lasts a certain time before the heart has recovered itself in so far that another contraction is possible. ENGELMANN objects to this, that the explosion brought about by the contraction in the molecular system of the muscle cell will destroy the stimulating matter in stock together with the other properties of this muscle cell, (irritability, contractility and conductive power); moreover did ENGELMANN show that the period of the formation of the stimulus can be changed independent of the irritability in the wall of the vena by chronotropic nerve influence. So we must assume that the systole destroys the stimulating matter and that every time the latter must again develop itself after every systole to active power. The law of the preservation of the physiological period of stimulation dominating the duration of the compensatory pause and all the important data come to light by means of "the method of the extra-systoles" for the frog's heart have been traced by CUSHNY and MATTHEWS (1) for the mammalian heart. These investigators showed that the mammalian heart obeys the same laws as the frog's heart, that its activity is dominated by the same fundamental properties of the fibres of the heart muscle, that the same theories hold good for both.

Only in one respect they found a difference: when the auricle is

artificially stimulated, the compensatory pause after the extra-systole is not as in the frog's heart truly compensatory but mostly of too short a duration. Sometimes it was completely compensatory, it was never entirely missing, it was generally shortened and then at any rate not equally shortened.

They say on this subject (l. c. page 226): „As long as the interval $A_s - A_c$ is of considerable length the compensatory pause in the auricle is truly compensatory, that is the interval between the last spontaneous contraction and the post-compensatory is equal to two auricular cycles. When however the stimulus falls earlier in the irritable period, no true compensation occurs, the post-compensatory contraction being premature, . . . when $A_s - A_c$ is short the compensation (of time W.) before the first natural contraction is always imperfect.”

The explanation of this difference is according to them: “either the contraction wave passes from the auricle to the great veins and there sets up a forced contraction which returning to the auricle causes the premature systole, or the irritability of the auricle gradually increases until it culminates in a contraction which is independent of the great veins and initiated in the auricular muscle itself. As to which of these two is the correct explanation we are unable to give any opinion and feel that it would be useless to balance probabilities before the movements of the great veins have been examined.”

Formerly I myself expressed the supposition, that the mammalian auricle might possess a greater automatic irritability, because in the phylogenetic development a part of sinus and vena would be taken up in the auricle.

H. E. HERING (2) has also been able to establish the difference described for the first time by CUSHNY and MATTHEWS; he says:

“The earlier the moment of stimulation falls in the irritable period of the auricle, the shorter the artificial bigeminus is (interval between last spontaneous and post-compensatory systole); the later it falls, the more the duration of the artificial bigeminus approaches that of two normal cardiac periods.” He continues: “the pause (after the extra-systole of the auricle) lasts longer according to the moment of stimulation falling earlier in the irritable period.” So here too he assumes the law of the conservation of the physiological period of stimulation: “aber die Beziehung ist keine so einfache wie am Ventrikel”.

We had all overlooked, that MACKENZIE (3) had become convinced already in 1894 after a careful analysis of the venous and liver pulse

that also in the human heart a "premature" contraction coming from the auricle is often succeeded by a too short compensatory pause. The possibility of distinguishing in this way between auricular and ventricular extra systoles had not escaped his attention.

When reflecting upon the consequences which extra systoles coming from the auricle must have on the action of the heart and the circulation of the blood of man, I found the following simple explanation of the above mentioned phenomenon, an explanation from which ensues that we have not got anything to do with a difference in principle between the frog's heart and the mammalian heart and that it is founded on an anatomic difference between the two hearts.

ENGELMANN (5) has shown that in muscular tissue of equal composition the stimulus to contraction is conducted also at an equal rate in all directions. So when an artificial stimulus is given to the auricle, a contraction stimulus and with it a contraction wave will pass from the stimulated point not only to the lower parts of the auricle and to the ventricle, but also to the higher parts of the auricle and to the vena cava, so to the place where normally the stimulus is formed and the contraction begins. ENGELMANN (6) has already pointed to the importance which this "antiperistaltic" movement may have for the action of the heart, CUSHNY and MATTHEWS have also seen the possibility of it.

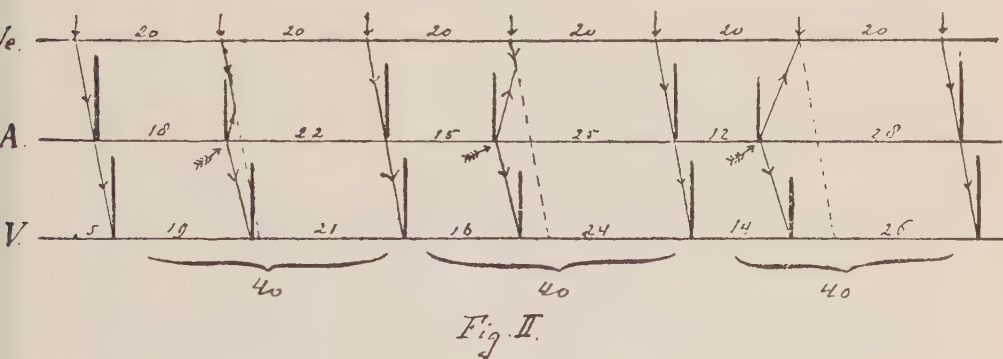
When a stimulus is applied late in the irritable period of the auricle, so just before the moment when the following physiological stimulus was to come from the vena cava, the stimulus (and the contraction) will not be able to reach the vena cava any more before the physiological stimulus has had its effect there: auricle and ventricle will obey the extra stimulus, the spontaneous contraction already begun will not go on, but the rhythm at the venae is not disturbed.

If the extra-systole sets in a little earlier, the extra contraction might reach the vena cava just at the moment that the physiological stimulus had developed to the necessary intensity; then also auricle and ventricle obey the extra stimulus, the physiological stimulus is neutralized or it finds the whole heart refractory, but here too the rhythm of the formation of the stimulus is not disturbed and the pause of auricle and ventricle is completely compensatory.

When however the auricle is stimulated still earlier, the extra contraction will reach the vena cava before the moment, in which the stimulus to contraction forming there, had attained at sufficient strength to cause a contraction. The stimulating matter found there at that moment will be destroyed by the extra contraction: from this moment

new stimulating matter is being formed and after a certain time equal to the normal period it will have obtained enough intensity to cause another contraction. So the following spontaneous systole will *not* fall in the moment it would have done so if an extra systole had not been set up, but just so much *earlier* as the extra contraction reached the vena cava *before* the moment in which the following spontaneous contraction would have occurred.

In the diagrams II and III an attempt has been made at making these observations clear for a particular case.

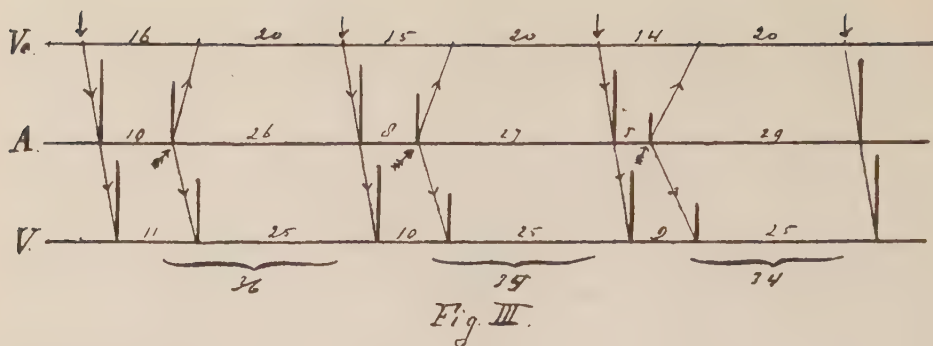


In fig. II the auricle is artificially stimulated respectively 18, 15 and 12 units of time after the previous spontaneous contraction; auricle and ventricle follow the extra stimulus; in the first two cases the extra contraction moving to the vena cava intercepted the spontaneous contraction coming from the vena cava. In the third case it arrives in the vena cava just at the same time as the physiological stimulus becomes active. In all these cases the rhythm remains undisturbed and the compensatory pause is complete for the auricle as well as for the ventricle: the interval between the systole preceding the extra systole and the one following it is double the period of the heart, in this case = 40.

In fig. III an earlier stimulation of the heart is shown, 10, resp. 8 and 5 units of time after the preceding systole the auricle is stimulated. The extra systole formed by the first stimulus arrives in the vena cava 4 units *before* the following spontaneous contraction.

The stimulating matter present at that moment is destroyed and a certain time = 20 has to pass before the stimulus has increased to sufficient strength. So the interval of the spontaneous contractions is not = 40 but = $16 + 20 = 36$.

According to the extra auricular contraction falling earlier, this



interval must become shorter, a fact which goes without saying, in fig. III resp. = 35 and = 34.

From this ensues, that when the stimulation is effected late in the irritable period the compensatory pause is complete and furthermore, the earlier the stimulation is effected the shorter the interval between preceding systole and following spontaneous systole.

Another influence is still at work, which also governs the length of the pause. The earlier the stimulation is effected in the irritable period of the auricle, the slower the stimulus is conducted through the wall of the heart, for the conductive power of the cardiac muscle returns but gradually after the preceding systole. So the interval $A_f - V_c$ will be longer according to the stimulus being effected earlier and as this interval also dominates the moment in which the stimulating material is destroyed by the induced extra contraction it will also influence the length of the auricular interval. In fig. III where the slower conduction when the stimulus is effected earlier is taken into account this influence is illustrated. And in this way it is to be explained, that the interval is longer after an auricular extra-systole according to the moment of stimulation falling earlier in the irritable period of the auricle following quicker upon the preceding systole.

The differences in length of the compensatory pause after stimulation of the auricle are in this way easily explained and it appears that the rules established for the amphibian heart hold good for the mammalian heart, in the sense however, as HERING says, that "die Beziehung keine so einfache ist".

The peculiar modifications in the course of the extra contraction when the auricle is stimulated, derived by MACKENZIE from the venous pulse, by CUSHNY and MATTHEWS from the tracings of the auricular movements, will probably find their explanation in the way in which, as is proved in fig. II, the contraction waves meet here in the auricular

wall and the differences will depend upon the spontaneous or the extra contraction being the most considerable.

The question must however now be put: why does a complete compensatory pause always (or almost always, ENGELMANN ⁶) follow the extra systole of the auricle in the amphibian heart and why in the mammalian heart only under certain conditions?

The answer may run as follows: In equally built up parts of the heart muscle the stimulus is also equally conducted to all sides, but where for whatever reason the state of the muscle fibres is not everywhere the same, the conduction of the stimulus will neither be the same. This is the reason that the conduction of the stimulus of the auricle on the ventricle, in general of one division of the heart on the other, takes place much slower than inside the wall of auricle or ventricle. When conduction takes place in the direction opposed to the normal, this distinction will not make itself less felt. And just as the slower conduction may be the cause that extra-systoles of the ventricle never recede quickly enough to have a disturbing effect on the rhythm of the great veins, the differentiation between veins, sinus and ventricle in the frog's heart will be the cause, that here a stimulation of the auricle is not quickly enough conducted through the transition places to disturb the rhythm at the venae cavae. Moreover this possibility seems so much the slighter, because in the frog's heart muscle fibres with a strong automatic irritability ascend high up in the vena cava and so cannot be reached so easily by an extra stimulus. As this differentiation of the cardiac muscle between vena cava and atrio-ventricular limit is missing for the mammals, it is no wonder that the disturbing influence on the formation of the stimulus at the vena cava occurs just in the mammalian heart.

If finally this explanation is the right one, the place where the auricle of the mammalian heart is stimulated, will have its effect on the length of the compensatory pause: perhaps it will be possible to establish for not too small hearts and where the conduction of the muscle has already somewhat slackened, that for auricular stimulation far from the vena cava the compensatory pause is longer or even complete, whilst the pause becomes shorter according to the auricular stimulation taking place closer to the vena cava. For such an experiment the stimulation would always have to be effected exactly in the same moment of the heart period, every time equally long after the preceding systole.

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Mathematics. — "*On the geometrical representation of the motion of variable systems*". By Prof. J. CARDINAAL.

1. In two communications ¹⁾ some theorems have been developed by me, relating to the motion of variable systems. Also in this subdivision of the doctrine of motion the method of the geometrical representation occurring so frequently in Mathematics can be applied. The following communication has in view to mention some particulars on this subject. The representation in question is treated ²⁾ by R. STURM. From this treatise I derive the short summary, which must needs appear here as an introduction to the subject.

2. In the quoted considerations two complexes of rays played an important part, namely the tetrahedral complex formed by the directions of the velocities of the points of the moving system and the rays of a focal system belonging to it; the latter consists for the motion of an invariable system of the normals of the trajectories of the points and for a projectively variable system of rays whose construction took a great part of the considerations. The purpose must be to obtain a simultaneous representation of complex and focal system; it will prove desirable to give the foremost place to the representation of the focal system.

3. Let thus be given the focal system \mathcal{A} situated in the space Σ . According to the method of SYLVESTER let us suppose two planes ξ and ξ' with two projective pencils of rays situated in them with their vertices X' and X situated on the line of intersection $\xi\xi' \equiv x$,

¹⁾ Proceedings of the Kon. Akad. van Wetensch., section of science, vol. IV, pages 489 and 588.

²⁾ Die Gebilde ersten und zweiten Grades der Liniengeometrie, I, p. 257.

x being an homologous ray of both pencils. The rays of \mathcal{A} are the transversals of two homologous rays of $(X\xi')$ and $(X'\xi)$.

Let us now take two sheaves of rays in the space Σ_1 with the vertices X_1 and X'_1 and establish a projective correspondence between these sheaves and the pointfields ξ and ξ' , in such a way that the pencil of planes through the axis $X_1X'_1$ is homologous to the pencils $(X\xi')$ and $(X'\xi)$. Let l be a ray of \mathcal{A} , cutting two homologous rays of $(X\xi')$ and $(X'\xi)$, to which in the homologous plane λ_1 a ray l_1 out of X_1 and a ray l'_1 out of X'_1 correspond; l_1 and l'_1 intersect each other in a point L_1 . This point is homologous to the ray l . So a projective correspondence is established between the points of the space Σ_1 and the rays of the focal system \mathcal{A} .

As is the case with every representation, also here the knowledge of its principal curve cannot be dispensed with. It is a conic X_1^2 through the points X_1 and X'_1 situated in a plane ξ_1 . Its points are homologous to the pencils of rays of \mathcal{A} situated in planes through x . The plane ξ_1 (principal plane) itself is homologous to x .

To an arbitrary pencil of rays of \mathcal{A} a right line corresponds cutting X_1^2 , to a hyperboloidic system of focal rays a conic having two points in common with X_1^2 , to a linear congruence belonging to \mathcal{A} a quadratic surface through X_1^2 .

4. Let a projectively variable moving spacial system be given; let as before $PQRS$ be the tetrahedron of coincidence of two successive positions and let the corresponding focal system \mathcal{A} be determined by PQ and RS as conjugate polars and the conic K^2 touching PR and PS in R and S . According to the indicated method the focal system can be represented in the space Σ_1 ; for the tetrahedral complex of the directions of the velocities, however, we need another representation, which can be taken in such a way that the same principal curve is retained; we shall succeed in this if we do not represent the complex itself, but its section with the focal system \mathcal{A} . This gives rise to a congruence (2,2) which we shall first investigate more closely.

5. Let A be an arbitrary point, α its focal plane; at the same time A is the vertex of a quadratic cone, geometrical locus of the directions of the velocities through A , but of which only one is the direction of velocity of A itself. This cone will cut in general α into two rays belonging to the congruence (2,2); in this way we can construct the whole congruence. By this we have determined the construction, but not the geometrical character of the congruence; this can be done in the following manner:

Let the direction of the velocity a of a point A intersect the plane of coincidence PRS in L ; now the focal plane of A intersects this plane in the polar p of L with respect to the conic K^2 . The rays of the complex, at the same time rays of the conjugate focal system, are situated in the focal plane α of A ; from this ensues that these rays intersect the plane PRS in two coincident points, at the same time conjugate with respect to K^2 ; so these rays will intersect K^2 and now ensues the theorem:

"The rays of the congruence (2,2), which is the section of the complex with the focal system, have a point in common with the conic K^2 ; so they are found as rays of A cutting K^2 ."

So the congruence (2,2) arising from this belongs to those congruences, not possessing a focal surface, but a singular or double curve¹⁾, geometrical locus of the first series of foci of the congruence.

6 The congruence can be constructed as a whole out of points of the conic K^2 ; for these points have the property of being the points of intersection not only of two but of a whole pencil of rays of the congruence (2,2), situated in the focal planes belonging to each of the points. These focal planes envelop a quadratic cone P^2 , with the vertex P ; so the congruence must touch the cone. From this ensues the following construction:

"Let a point A be taken on K^2 , the focal ray PA be drawn, cutting K^2 for the second time in A' . Let the two tangential planes to P^2 be brought through PA ; each of these planes contains a pencil of rays of the congruence, the vertex of one pencil being A , of the other A' ."

7. We now proceed by giving some visible properties of the congruence (2,2).

a. The two foci of each ray are the points of intersection with K^2 and the point of contact with P^2 . The focal surface of points becomes P^2 ; the focal surface of tangential planes consists of the tangential planes of K^2 .

b. All rays of the congruence (2,2) belonging to a congruence of rays (1,1) of A cut two conjugate polars of A , and cutting at the same time K^2 they form a ruled surface of order four with a simple conic and two double lines.

c. The rays of the congruence (2,2), lying on a hyperboloid of

¹⁾ Congruences of this type are ranged in the "Index du répertoire bibliographique des sciences mathématiques" under *N° 162* and placed by R. STURM in a separate division; see "Liniengeometrie", II, p. 323.

\mathcal{A} , pass through the points of intersection of the latter with K^2 ; so they are four in number.

d. Let K^2 be real and let P be situated within K^2 ; all focal rays through P , the focal point of plane PRS , now cut K^2 ; so all pencils of rays are real. If P lies outside K^2 two tangents out of P can be drawn to K^2 ; these tangents are the lines of intersection of the cone P^2 with plane PlS . The planes touching P^2 according to these lines of intersection are focal planes, in which two pencils of rays have coincided; rays through P , not cutting K^2 , give rise to imaginary pencils of rays of the congruence (2,2). Further ensues from this:

“If K^2 is real and all the vertices of the tetrahedron of coincidence likewise are real, the congruence (2,2) is built up of real and imaginary pencils of rays, where as a transition two are double ones; if K^2 is real but the vertices R and S are imaginary, all the pencils are real.”

e. The cases in which K^2 is imaginary, or also those in which all the vertices of the tetrahedron of coincidence are imaginary, do not give real congruences; so they are not under consideration.

8. We now pass to the representation of the congruence (2,2) by which the image is obtained of the connection of focal system and tetrahedral complex.

a. The congruence containing ∞ pencils of rays which are represented in Σ_1 by straight lines having a point in common with X_1^2 , the whole congruence is represented by a ruled surface passing through X_1^2 . To a straight line l_1 in Σ_1 a hyperboloidic system of focal rays corresponds, which has four points in common with K^2 ; so it contains four rays of the congruence and the representing surface S_1^4 of the congruence (2,2) is a ruled surface of order four.

b. An arbitrary pencil of focal rays of \mathcal{A} contains two rays of the congruence; the straight line in Σ_1 corresponding to them cutting X_1^2 has another two points in common with S_1^4 ; so X_1^2 is a double conic of S_1^4 .

c. To the pencil of rays in Σ with P as vertex and PRS as plane a straight line p_1 in Σ_1 corresponds, cutting X_1^2 . Each ray of the pencil P/PRS belonging to two pencils of rays whose vertices are points of intersection with K^2 , in all points of p_1 two generators of S_1^4 concur; from this follows that S_1^4 is a ruled surface having as double curve a conic with a straight line cutting it; with this the type of S_1^4 has been established.

9. A closer acquaintance with the form of S_1^4 is obtained by tracing the pinchpoints on the double curve; there can be two of them on p_1 and two on X_1^2 . Those of p_1 depend on the position of P with respect to K^2 .

a. Let P be outside K^2 . When a ray through P cuts K^2 in two points, we get two pencils of rays of the congruence, to which two real generators of S_1^4 correspond, concurring in a point of p_1 . For the tangential lines out of P to K^2 these two generators coincide, so the point of S_1^4 , from which they are drawn is a pinchpoint; so for this position there are two real pinchpoints on p_1 ; from this ensues:

"If P lies outside K^2 , p_1 has one part appearing as double line and another which is isolated; two pinchpoints separate these two parts."

b. Let P lie within K^2 . All focal rays through P cut K^2 ; there are no tangents to K^2 , so there are no pinchpoints on p_1 . So the double line p_1 is in its whole length really double line.

Besides the pinchpoints on p_1 the surface S_1^4 has also pinchpoints on X_1^2 . To find these we must keep in view that the points on X_1^2 correspond to the pencils of rays whose vertices lie on $XX' \equiv x$, which are thus situated in planes through x . Let γ be a plane through x and C its focal point; the pencil of rays $(C\gamma)$ has two rays cutting K^2 viz. the two rays connecting C and the points of intersection B and B' of γ and K^2 . These two rays are represented in Σ_1 by a single point B_1 of X_1^2 . Now CB belongs still to another pencil of focal rays, viz. to the pencil whose vertex is B and whose plane is the plane $CBP \equiv \beta$. The latter pencil belongs to the congruence (2,2) and is thus represented by a straight line through B_1 lying on S_1^4 . In a similar way it appears that also a second straight line of S_1^4 passes through B_1 , namely the one which is represented by the pencil of rays $(B'\beta')$ lying in plane $CB'P$. Now again two principal cases may occur:

a. x cuts the plane PRS in a point T outside K^2 . The pencil of rays T lying in this plane has rays cutting K^2 in two points, touching K^2 or having two imaginary points in common with K^2 . In this case these are parts of X_1^2 through which two generators of S_1^4 pass, which have thus to be regarded as points of a double curve, and parts which are isolated; the transition is formed by two pinchpoints, through which two coinciding generators pass; and these last correspond to the pencils of rays, having their vertices on the tangents drawn from T to K^2 .

b. The above mentioned point of intersection T lies within X_1^2 . All rays through T cut K^2 ; through each point of X_1^2 two generators pass, so the whole conic X_1^2 is a double curve.

10. Among the particular sections of S_1^4 the conics of this surface come into account. These conics have two points in common with X_1^2 ; so (3) to these must correspond in Σ hyperboloidic systems of focal rays of A . These can be constructed in the following way:

Let again a point A be taken on K^2 , its focal plane α be determined, moreover the second point of intersection A' of α with K^2 and the focal plane α' of A' . If now a pencil of rays be drawn in α' through A (which rays are not focal rays) and likewise through A' in α , the pencils (A, α') , (A', α) consist of conjugate polars of A between which a projective correspondence is established by means of the focal rays. In connection with X_1^2 each pair of conjugate polars causes a hyperboloidic system of focal rays to appear. These two pencils generate them all, so their number is ∞ .

11. Finally a few particular cases ask for our attention.

a. The line of intersection x cuts the plane PRS in a point of the tangent plane PR . The pencil of focal rays in the plane PR has as vertex this point of intersection; to this pencil corresponds a pinchpoint on X_1^2 , but at the same time this pencil of rays has moreover a ray in common with the pencil of rays in the focal plane of the point R ; so the obtained pinchpoint is at the same time a point of ρ_1 ; from this follows that in the point of intersection of X_1^2 and ρ_1 two pinchpoints have coincided; so through this point only a single generator of S_1^4 can be drawn.

b. Application to the motion of an invariable system. In this case K^2 is imaginary (the imaginary circle in the plane at infinity); so the congruence (2,2) consists entirely of imaginary rays. The pencil of rays P/PRS , however, remains real; so the representation in Σ becomes an imaginary ruled surface S_1^4 with real double curve consisting of a straight line and a conic intersecting it. The same observation can be made for other cases where K^2 becomes imaginary.

c. Another particular case occurs when the ray $XX' \equiv x$ is taken in such a way that it cuts the conic K_1^2 ; by doing so the character of the congruence does not change, but its representation does. If we now consider a pencil of rays in a plane brought through x , it is apparent that always one of the two rays of congruence to K^2 coincides with x . Of the two rays cutting in Σ_1 the double conic X_1^2 only one is situated on S_1^4 , the other one passes into a ray situated in ξ_1 ; from this follows:

"When the focal ray x cuts the conic K^2 the surface S_1^4 breaks up into ξ_1 and a cubic ruled surface S_1^3 of which ρ_1 is a double line; so this gives a simpler representation of the congruence (2,2)

Physiology. — “*A new law concerning the relation between stimulus and effect.*” By Dr. J. K. A. WERTHEIM SALOMONSON, communicated by Dr. C. WINKLER. (Communication IV).

In three papers, bearing the title “a new law concerning the relation between stimulus and effect I, II and III, I have tried to prove that by increasing a stimulus, the effect too will increase in a definite manner.

The relation was expressed by the formula

$$E = A (1 - \epsilon^{-B(R-c)}) \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

In deducing this formula I assumed that the transformation of chemical substance caused one and only one well-defined effect.

In most cases however from such a transformation several consequences will result, constituting together the total effect: e.g. a mechanical, a thermal, a chemical, an electrical effect may be caused simultaneously by some changing of the protoplasma.

The question arises, whether our mathematical expression may be applied as well to the different parts of an effect as to the total effect. In order to obtain an answer to this question, we have to consider again the differential equation:

$$-dE = BE dR \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

expressing, that by an infinitesimal increment of stimulus an infinitesimal proportional part of the transformable substance was transformed, and at the same time stating the quantity of this transformation. The quantity $-dE$ represents the increment of the effect. In the case of the effect being composed of several different parts,

the same equality will prevail for any of them, e.g. the $\frac{1}{n}$ part, and so we shall obtain for a *partial* effect the equation

$$-\frac{1}{n} dE = BE dR \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

in which $n > 1$.

From this formula we get the expression

$$E = a \{1 - \epsilon^{-nB(R-c)}\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

wherein a represents another constant than A , and wherein n is a number larger than 1.

This formula for a partial effect is identical to the formula for a

total effect the only difference being that the exponential constant in the case of a partial effect is larger than in that of a total effect.

The muscle may be taken as an example. Every contraction brings about a mechanical effect, whilst at the same time an electrical response is given. Finally the production of heat may be taken for the total effect, at any rate in the case of isotonic or isometric contractions where the mechanical effect is afterwards converted into heat. Thence we are justified in presuming that our statement about the formulæ for total and partial effects, may be applied to the thermal effect and mechanical effect of muscle-contractions.

I have tried to ascertain whether the numbers, given for the thermal-effects by different authors are in accordance with our law.

In DANILEWSKY¹⁾ I found several series of numbers, from which the following tables were calculated

TABLE I.

DANILEWSKY, l. c. pag. 184.

Isometrical contraction. Initial
load 40 gram fig. 1. $A = 23 \quad B = 0.03 \quad C = 18.$

R	E_w cal.	E_w observ.
20	1.54	1.7
30	6.97	4.5
40	11.09	11.4
50	14.18	16.2
80	19.38	19.2
100	21.00	19.8
300	22.98	20.5
600	23.	22.
800	23.	24.2

In this table, as in the following R represents the magnitude of the stimulus; E_w observ. the thermal effect as observed by DANILEWSKY.

¹⁾ B. DANILEWSKY. Ergebnisse weiterer thermodynamischer Untersuchungen der Muskeln. V. e. A. FICK. Myothermische Untersuchungen 1889.

E_w calc. the thermal effect, as calculated with the constants given at the head of each table.



TABLE II.

Ib. Initial load 80 Gr. fig. 2.

 $A = 24.2$ $B = 0.0324$ $C = 20.$

R	E_w calc.	E_w observ.
30	6.7	6
50	15.3	18
100	22.4	21.7
300	24.2	24.8

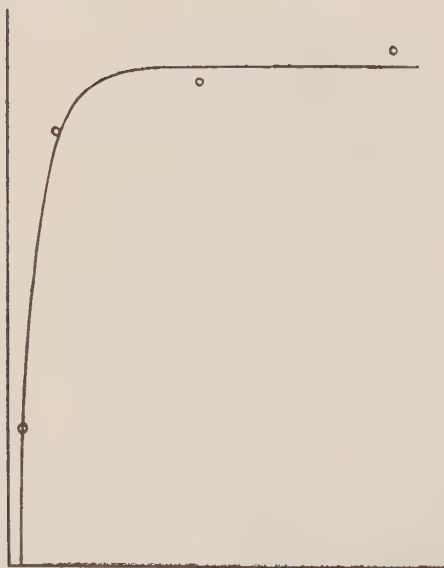


TABLE III.

Ib. Initial load 300 Gr.

fig. 3.

 $A = 20.8$ $B = 0.0217$ $C = 16.4.$

R	E_w calc.	E_w observ.
30	5.3	5.5
100	17.4	18
400	20.7	20
800	20.8	21.5

The first of the next-following tables, which are much more important, is also taken from the experiments of DANILEWSKY l.c.,

whilst the observations in the 5th and 6th table have been published by NAWALICHIN¹⁾: the school of HEIDENHAIN and that of FICK are both represented.

The higher importance of the series given hereafter, consists chiefly in the fact of their having served to determine as well the mechanical response as the thermal effect with stimuli of increasing magnitude.

In the series of DANILEWSKY a double thigh-muscle-preparation of the frog after the method of FICK was employed, whilst NAWALICHIN made use of a single gastrocnemius.

The muscle contracted isotonically, whilst simultaneously the thermal and the mechanical effect of each contraction, were recorded. As it has been proved with sufficient accuracy in our first papers that our formula may be applied to isotonic twitches, these may now serve us as a means of control.

In the following series the magnitude of stimulus is again indicated in the first column by R . The second column contains the calculated height of twitch, the third column the observed height; the fourth column the calculated and the fifth the observed thermal effect. The constants A_w , B_w and C_w were used for calculating the thermal effects, the constants A_h , B_h and C_h for calculating the heights of the contractions.



TABLE IV.

DANILEWSKY l. c. Load 60 Gr. fig. 4.

$A_h = 40$ $B_h = 0.05$ $C_h = 14.4$
 $A_w = 14.55$ $B_w = 0.02$ $C_w = 14.4$

R	E_h calc.	E_h observ.	E_w calc.	E_w observ.
20	9.77	9.8	1.54	0.7
30	21.66	27.7	3.90	4
50	33.25	33	7.41	7.7
100	39.45	39.1	11.92	11.1
300	40.00	40	14.50	14.5

¹⁾ NAWALICHIN, Myothermische Untersuchungen. Pflüger's Archiv, Bd. 14, p. 297.

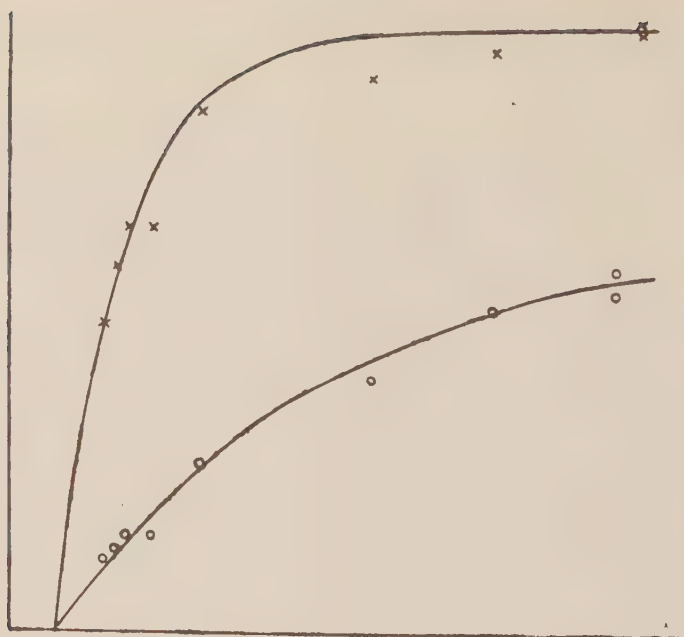


TABLE V.

NAWALICHIN l. c. pag. 297. Load 30 Gr. fig. 5.

$$A_h = 6.25 \quad B_h = 0.0036 \quad C_h = 205$$

$$A_w = 17. \quad B_w = 0.00085 \quad C_w = 205$$

R	E_h calc.	E_h observ.	E_w calc.	E_w observ.
400	3.17	3.2	2.60	3
450	3.66	3.8	3.20	3.5
500	4.08	4.2	3.78	4
600	4.74	4.2	4.81	4
800	5.52	5.4	6.75	7
1500	6.18	5.7	11.34	10.5
2000	6.23	6	13.30	13.5
2500	6.25	6.2	14.60	15
2500	6.25	6.3	14.60	14

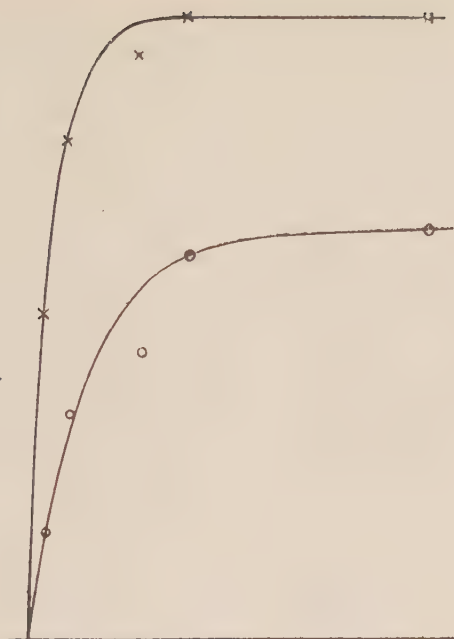


TABLE VI.

Ib. Load 90 Gr. fig. 6.

$$\begin{array}{lll}
 A_h = 6.5 & B_h = 0.0185 & C_h = 660 \\
 A_w = 17.15 & B_w = 0.008 & C_w = 660
 \end{array}$$

R	E_h calc.	E_h observ.	E_w calc.	E_w observ.
700	3.40	3.5	4.70	4.5
750	5.27	5.3	8.80	9.5
900	6.42	6.1	14.61	12
1000	6.50	6.5	16.00	16
1500	6.50	6.5	17.10	17

Considering that the degree of accuracy with which the thermal effects were measured is not very high, we have some cause for satisfaction about the results of our calculations. Though only a first approximation has been effected throughout all these series, the errors remain wholly within the limits of the mean errors of observation. Moreover in some cases it is even possible to apply a correction.

Looking at series VI, we see immediately that the observed numbers

corresponding to the stimulus 900 are rather too small, as well for the height of twitch as for the heat-production. Calculating from the observed lifting-height the corresponding magnitude of stimulus, we find 810 instead of 900. Now taking this number 810, to calculate the heat-production, we obtain 12, in perfect accordance with the observation. The supposition that the number 900 is an error and that 800 was meant is not very hazardous.

From the communicated series we may draw firstly this conclusion that the heat-production, considered as total effect, increases virtually with increased magnitude of stimulus in the manner indicated by the established formula.

In the three last series B_w , the increment-constant for the thermal effect, proved to be always smaller than the B_h corresponding to it, a fact predicted already in our deduction. We found for the number $n = \frac{B_h}{B_w}$ in series IV, V and VI the value 2.5, 4.23 and 2.31. Though of course even by this fact our deduction may not be deemed absolutely proven, it nevertheless affords a valuable support for considering the deduction proposed by me as a most useful working-hypothesis.

Bacteriology. — “*On a colourless bacterium, whose carbon food comes from the atmosphere.*” By Prof. M. W. BEIJERINCK and A. VAN DELDEN.

We give the name of *Bacillus oligocarbophilus*¹⁾ to a colourless bacterium, whose carbon nutrition in the dark (and likewise in the light), takes place at the expense of a not yet well-known atmospheric

¹⁾ It is probable that W. HERAEUS (Ueber das Verhalten der Bacterien in Brunnenwasser sowie über reducirende und oxydirende Eigenschaften der Bacterien. Zeitschrift f. Hygiene, Bd. I, pag. 226) already in 1886, has had cultures of *B. oligocarbophilus* before him. He says the following: „Ausserordentlich auffallend war das Ergebniss dieser Versuche in der Hinsicht, dass eine Vermehrung der Bacterien in einer Flüssigkeit eingetreten war, welche keine organische Verbindungen sondern nur Salze enthielt. Ein unansehnliches, kaum sichtbares Pünktchen von Bacterienzoogloeën hatte sich im Verlaufe vom zehn Tagen so stark vermehrt, dass die ganze Oberfläche der Lösung von einer dicken Haut bedeckt war.” Analytical results are not given, and the remark makes the impression of being accidental and is lost among insignificant observations. — WINOGRADSKY’s statement, concerning the accumulation of organic carbon in nitrifying solutions, evidently refers likewise to this microbe, but his description suffers of indistinctness (Annales de l’Institut Pasteur, T. 4 pg. 270 et 462, 1891).— In the experiments of GODLESKI (Bulletin international de l’Académie d. sc. d. Cracovie, Dec. 1892 pag. 408 et Juin 1895 pag. 178), the vanished CO² is not, as he thinks, absorbed by the ferments of nitrification but by the Mg O . Mg CO³.

carbon compound (or compounds), from which the energy, wanted for the vital processes, is also derived ¹⁾.

The culture of this bacterium on solid media or in nutrient solutions, containing soluble organic substances has not yet succeeded, which may, of course, have been caused by an erroneous choice of these substances. On the other hand, pure cultures on solid and in liquid substrata, without soluble carbon compounds, are easy to be made.

1. CRUDE CULTURES OF *BACILLUS OLIGOCARBOPHILUS*.

Bacillus oligocarbophilus is obtained by the following accumulation experiment, which, because of the purity of the thereby resulting vegetation, may be called a "perfect accumulation experiment."

Into a large ERLÉNMEYER-flask a thin layer is introduced of a nutrient liquid of the same composition as used for the water culture of higher and lower green plants, but with alkaline instead of acid reaction.

One takes for instance:

Distilled water	100
Kaliumnitrate	0.01 to 0.1
Dinatriumphosphate	0.02
"Mineral solution"	1 drop.

This "mineral solution" contains in one drop:

8	Mgrms	MgSO ₄ . 7 H ₂ O
0.05	"	MnSO ₄ . 4 H ₂ O
0.05	"	FeCl ₃ . 3 H ₂ O

If from this liquid nitrogen, phosphor, kalium or magnesium is left out, special experiments have proved, that no, or but an insignificant growth is obtained. As to the necessity of the likewise added elements sulphur, manganese and iron, there still exists some doubt.

The inoculation is made with a not too small quantity of garden-soil, the flasks are closed with a cotton plug, or with filter paper, without impeding the entrance of air by diffusion, and the culture is left in the dark at 23—25° C. After two or three weeks, the fluid, which itself remains perfectly clear, is seen to cover with a thin, white, or feebly rose-coloured, very dry film, difficult to moisten, and macroscopically resembling a *Mycoderma*-film, but consisting of minute bacteria, microscopically often invisible without staining, and sticking together by a slimy substance. This is *Bacillus oligocarbophilus*.

¹⁾ We also found another, rarer species, belonging to the genus *Streptothrix* CONN, with corresponding properties. It will not, however, be further discussed here.

The growth of the film continues for months, whereby a considerable accumulation of organic carbon may be observed, which is not only visible to the naked eye by the vigorous bacterial growth, but can also be proved by direct weighing, and by a comparison of the permanganate numbers found before and after the experiment, of which some instances are given below.

As there is reason to admit that our bacterium is generally distributed in garden-soil, and was without doubt always present in the crude material used for the inoculation, the failing of the film-formation in some of the flasks must necessarily result from the chosen culture fluid being less favorable to the feeble germs and not allowing their growth. So we observed that water, distilled in a copper apparatus, caused many more failures than when distilled in glass; we therefore afterwards always used the latter. In other cases monads, which immediately devoured the bacteria, were cause of the failure; by transfers and by the use of pure cultures, these voracious organisms could be rendered harmless or removed. When the distilled water is replaced by tap-water, the number of flasks remaining without growth after inoculation with the same quantity of garden-soil is much smaller.

If once a pellicle has formed, transfers into the said culture liquid, prepared either with distilled or with tap-water, come easily and without exception to development.

2. SOURCE OF NITROGEN REQUIRED.

In the above mentioned nutrient liquid we have chosen kaliumnitrate as source of nitrogen. As well, however, kaliumnitrite or some anorganic ammonium salt may be used. Very good results were obtained with:

Distilled water	100
Ammonium sulphate (or NH_4Cl)	0.01—0.1
Dikaliumphosphate	0.02
"Mineral solution"	1 drop

and with:

Distilled water	100
Kaliumnitrite	0.01—0.1
Dikaliumphosphate	0.02
"Mineral solution"	1 drop.

As both these liquids answer to the conditions of life of the microbes of nitrification, the formation of nitrite or nitrate is actually to be observed when using them, and when inoculating with garden-soil or with crude cultures. With the easily produced pure cultures

of *B. oligocarbophilus*, of which more below, a good development of the film is possible, by which experiment it can at the same time be proved, that this microbe itself does not nitrify. Hence, ammonium salts or nitrites, added to excess can, even for a year or longer, continue unchanged under the luxuriantly growing pellicle of *B. oligocarbophilus*, whereas, in the presence of nitrifying ferments, they completely disappear in a few weeks, being then found back as nitrates. If the ferments of nitrification alone are present, there is no question of film-formation and the nutrient solutions remain perfectly clear.

Not only the nature of the nitrogen-furnishing substances, but also their quantity can in these experiments, as already inferred in the recipes, vary between fairly wide limits, and the same may be said concerning the conditions for the water culture of higher and lower green plants. The limits allowable for *B. oligocarbophilus*, have not yet been precisely fixed, but they certainly have a broader range for this organism (circa 0.1—10 pro mille) than for the higher plants (0.5—5 pro mille).

By many experiments it was established, that in absence of kalium, phosphor, and magnesium, a still slighter growth occurs, than when no nitrogen compounds are given. Evidently *B. oligocarbophilus* finds in the atmosphere, in a condition fit for nutrition, a quantity of nitrogen, which, although insufficient, should not be overlooked.

If the distilled water in the artificial solution is replaced by tap-water, a somewhat higher rate of organic substance is produced. As in tap-water a small quantity of nitrogen compounds occur, — here, at Delft, about 0.4 milligrams of combined nitrogen per litre, — whilst it contains the other necessary elements (phosphor and kalium, of course, excepted) in an obviously favorable form for the nutrition of our mikrobe, one can simply use for its culture:

Tap-water	100
Dikaliumphosphate	0.02.

It should, however, be kept in view, that the productivity in bacterial substance, in consequence of the film formation, is not determined by the volume, but chiefly by the extent of the surface of the medium, which is in free contact with the air. Hence, in a very thin layer of tap-water, the nitrogen may soon be consumed, whereas, with the same amount of nutrient liquid, but with a smaller surface, consequently in a thicker layer, the provision of nitrogen will suffice for a longer time. Therefore, in order to obtain from a flask of determined size, the maximum production of *B. oligocarbophilus*, a

nitrogen compound should be added when a small quantity of tap-water is used, which addition is not necessary when cultivating in a greater quantity in a flask of the same size.

3. PURE CULTURE.

Our bacterium does not grow at all or only to a slight extent on the commonly used bacteriological media, these containing too much organic food. But it is easy to produce pure cultures on solid media, when observing the same precautions which I described in the Meeting of the Academy of 27 June 1892 for the pure culture of the ferments of nitrification on agar-plates¹⁾, and to which I referred in the Meetings of 30 March 1901 (Proceedings p. 586) and 25 May 1901 (Proceedings p. 5) when discussing the culture conditions of the oligonitrophilous Cyanophyceae.

In all these cases it is necessary as completely as possible to remove all soluble organic substances from the solid medium, which is to be effected by a prolonged washing with distilled water. The agar thus prepared, with the required nutrient salts, for instance in the proportion:

Distilled water	100
Agar	1.5
K ₂ HPO ₄	0.01
KNO ₃ (of NH ₄ Cl)	0.01

is boiled and plated, and used for strew-or streakcultures originating from a film of *B. oligocarbophilus*. Very soon the common saprophytic bacteria which never lack in the film, are seen to develop on the plate and when these by their growth and respiration have consumed the soluble carbon compounds, which were not yet removed from the agar by the extraction with water, *B. oligocarbophilus* itself begins to grow. This is usually the case after 14 days. Then, however, the colonies become easily recognisable, our bacterium being the only species which in the given circumstances can feed on the atmospheric carbon, and so go on growing, whilst the growth of all other species soon comes to a stop.

Even the colonies of the nitrifying ferments, which, as I have demonstrated before (l. c.), can grow fairly well on this medium, when instead of nitrate an ammonium salt is used, remain very small, never exceeding 1 mM. or less. On the other hand, the colonies of *B. oligocarbophilus* attain dimensions of 1 cM. and more and may then easily be transferred in a pure condition into test-tubes

¹⁾ Nature, Vol. 46, pag. 264, 1892.

on the said medium. They grow on the agar as thin, snow-white or rosy-tinted, very dry, flatly extended layers, which strongly remind of the pellicle floating on the liquid.

Also on silica plates, prepared in glass dishes, which, after extraction of the chlorides are soaked with a nutrient solution, *B. oligocarbophilus* can produce very fine cultures, appearing after some weeks, as snowwhite colonies with indented margin, and which by a right selection of the salts, can finally spread over the whole plate. Then the remarkable phenomenon is observed, that the silica liquefies a little in the centre of the colonies and sinks in by evaporation.

The silica plates are made as follows. A commercial solution of potassium silicate, diluted with a known quantity of water, is titrated with normal hydrochloric acid. As the solidification is much favoured by an alkaline reaction, a complete neutralisation at the preparation of the plate should not occur, and as a plate, with a high percentage of silica, contracts strongly after coagulation, and expresses much water, the dilution must be sufficient for this contraction to be delayed. Into a small beaker-glass was introduced, in a certain case, 5 cM³ of potassium silicate diluted with 25 cM³ of water, and into a second glass the required quantity of hydrochloric acid, amounting to 10 cM³ of normal acid. The acid is mixed with the diluted silicate and the mixture poured into a glass dish. The solidification delays the longer as the mass is more diluted, but it is easy, after some practice, to make very solid plates. The plate is first freed from the chlorides by streaming tap-water, then washed out with boiled water, and afterwards treated with the solution of nutrient salts. When these have sufficiently diffused into the plate, the glass dish is gently warmed at the underside, until the adhering water has evaporated and the plate shows a "dry", glossy surface. The surface is flamed in the Bunsen-burner, by which only a partly but sufficient sterilisation is to be attained.

Not only *B. oligocarbophilus*, but also the ferments of nitrification grow on this medium very well. By mixing of the diluted solution of the silicate with chalk, magnesium carbonate, or ammonium-magnesium phosphate, snow-white plates may be obtained, which are particularly fit for the culture as well of all these microbes as of several lower algae. Even earth-diatoms, of the genus *Nitzschia* will grow thereon.

Once more it must be observed, that in the silica plates organic substances must be absent, even fragments of cork, fallen into the silicate solution, may disturb the experiment.

The pure cultures, obtained on agar or silica plates, are as well fit

for the further experiments on liquid media as the crude cultures, of which many experiments, continued for years, have convinced us. Every thought of symbiotic relations on which the carbon assimilation by our bacterium might repose is thereby excluded, so that at least the biological side of this part of our problem is clear.

Concerning the further properties of our bacterium in pure cultures, we can be brief. In the films, as well as on in the colonies on the solid media, it consists of minute, thin and short rodlets, probably always immobile. They are ca. $0.5\ \mu$ wide and $0.5-4\ \mu$ long. The length however is very variable and frequently particles are seen $0.5\ \mu$ wide and $0.7-1\ \mu$ long. Often, when not using reagents, such as dyeing substances or acids, no structure at all is to be observed, neither in the colonies nor in the flowing pellicle, but the bacteria at once become visible by staining the preparations. The thick cell-walls form the chief constituent of the colonies; albuminous matter is only present in a slight quantity in this bacterium.

4. THE NUTRITION WITH ATMOSPHERIC CARBON.

A good appreciation of the carbon accumulation may be had as well by a direct weighing as by the permanganate method.

For both determinations it is possible, to suck off the fluid, which is practically free from bacteria, wholly or partly from beneath the film, so that the quantity of the culture material, destined for the filtration or the determination of the permanganate number, is not too voluminous.

In our experiments there only resulted a precipitate of calcium-phosphate or calciumcarbonate, when we had used our tap-water, which is rich in lime, and when kaliumphosphate to excess had been added. These precipitates can, however, be dissolved beneath as well as in the film by dilute acid, and then the acid can be expelled by further washing. The film is so dry and wetted with so much difficulty, that all these manipulations may be effected without much loss of material.

The permanganate number was determined after KUBEL's¹⁾ method.

In relation to the quantity of organic matter found by direct weighing or by the permanganate method and formed from the atmospheric carbon, the following should be well observed.

As *B. oligocarpophilus* grows only on the free surface of the

¹⁾ TEMANN-GÄRTNER'S Handbuch der Untersuchung der Wässer, 4c Aufl. pag. 255 1895.

medium, and not in the depth, the thickness of the layer of the nutrient solution and consequently its volume, is, as already observed, actually indifferent. That is to say, by enlarging the surface of the solution, a bacterial film of any dimensions is to be obtained, which circumstance is of importance for appreciating the productivity of a certain quantity of a nutrient solution, the more so as the thickness of the bacterial film is usually only one cell-layer. How very thin the required thickness of this layer can be, growth being still possible, may be derived from the fact, that, especially when using distilled water with nutrient salts, the film can mount at the apparently dry glass-wall from 1 to 1.5 decimeter high, and not seldom extends on it nearly to the cotton plug. Only in certain vinegar bacteria I observed the same.

As it seems that our bacterium forms no compounds prejudicial to its growth, so the only circumstance, which governs its increase relatively to a given volume of liquid, provided its surface be of a sufficient extent, is the lack of one or more elements necessary for the nutrition. Carbon cannot be among the number, our experiments being made with free entrance of air.

Although it is thus established, that only the number of bacteria, produced in a certain time per surface-unit, indicates the rate at which the atmospheric carbon is assimilated, we will yet give the quantities in relation to the volume of the solution, because then a comparison can be better made with the numbers found by other authors for polluted waters.

5. HOW MUCH CARBON IS ASSIMILATED.

First we determined by an experiment, in which, after vigorous shaking, a culture was divided into two equal portions, how much one half contained at direct weighing, of bacterial substance, whereas the other half was titrated with kaliumpermanganate. We used for this a three months old culture on:

Tap-water	100
Na_2HPO_4	0.02
KCl	0.02
KNO_3	0.02

The film from the part, destined for the weighing, was separated from the liquid by filtration, washed out on the filter with strongly diluted hydrochloric acid, and subsequently with distilled water, to remove the chlorids. Subsequently the filter with the film was

dried, first at 40° — 50° C. and then at 100° C., until the weight remained constant. So we found that per litre 180 milligrams of bacterial matter were produced, and that, after deduction of 14 milligrams, used by a litre of our tap-water itself, the corresponding permanganate number was 94. We can thus, with an accuracy sufficient for our purpose, accept that the relation between the two figures is as 2:1, that is to say, that the doubling of the permanganate number gives the weight of the dry bacterial substance, and, as this latter number is much more quickly to be found than the weight, we have contented ourselves with it in most of our further determinations.

We shall now give some more figures. Like the preceding they all relate to bacterial films produced in ERLÉNMEYER-flasks on 100 cm^3 liquid with a free liquid-surface of about 80 cm^2 .

By weighing we found in one case on:

Tap-water	100
KCl	0.02
KNO_3	0.02
K_2HPO_4	0.04

after 5 months' culture 235 milligrams per litre. On:

Distilled water	100
KCl	0.02
KNO_3	0.1
K_2HPO_4	0.02
"Mineral solution"	1 drop

after 5 months 220 milligrams per litre.

Some numbers, found by the permanganate method follow, and in the first place some relating to tap-water.

The greatest production which we had, was obtained with tap-water $0.02\text{ K}_2\text{HPO}_4$ and 0.02 KNO_3 , after a year's culture and amounted to 250 mgrs. of permanganate per litre, nearly corresponding with $250 \times 2 = 500$ milligrams of dry bacterial substance.

After a shorter time the production is likewise smaller; so we found in a culture on:

Tap-water	100
Na_2HPO_4	0.02
KCl	0.02
KNO_3	0.02

after 5 months' culture (January to May) 202 mgrs. of permanganate, corresponding with 404 mgrs. of bacterial matter per litre.

If the tap-water was replaced by distilled water, the production of dry organic substance was commonly smaller, which cannot, however, result from the nutrition by substances in the tap-water, oxidisable by kaliumpermanganate, for the 14 mgrs. of permanganate, which our tap-water consumed per litre, we found quantitatively back, at the end of the cultivation period, in the clear liquid beneath the pellicle of *B. oligocarbophilus*, which liquid can easily be sucked off with a pipette, without any considerable bacterial contamination. Moreover the experiments with distilled water have likewise exhibited great divergency in production, and though the cause has not been established with perfect certainty, we still think it probable, that these differences result from the greater or smaller density of the cotton plugs, by which the speed of air entrance is greatly influenced. We base this supposition on results obtained with flasks, only differing in the width of the mouths, and to which we shall refer later. It is furthermore certain that we have not to do here with the infection of other bacteria, or with monads, for the pure cultures displayed as considerable divergency as the crude ones. Neither can the chief cause be attributed to a change in percentage of the air in gaseous carbon compounds, the differences being observed simultaneously in cultures placed side by side in the same locality.

But we now give some further numbers. In an experiment with:

Distilled water	100
K_2HPO_4	0.02
KNO_3	0.1
KCl	0.01
"Mineral solution"	1 drop

sterilised and inoculated with a pure culture of *B. oligocarbophilus*, were found, after 37 days' cultivation (2 Jan.—15 Febr.) at 23° C., 66.6 mgrs. of permanganate, corresponding with circa 133 mgrs. of dry bacterial substance per litre.

In another experiment with:

Distilled water	100
Na_2HPO_4	0.02
KNO_3	0.01
"Mineral solution"	1 drop

likewise sterilised and after a culture of 40 days, at 23° C. the permanganate number amounted to 60 mgrs., corresponding with 120 mgrs. of dry bacterial matter per litre.

In a third case in:

Distilled water	100
K_2HPO_4	0.02
$(NH_4)_2SO_4$	0.02
Na_2CO_3	0.01
"Mineral solution"	2 drops

after cultivating from 5 May to 1 Dec., 155 mgrs. of permanganate per litre were found.

In a culture in:

Distilled water	100
Na_2HPO_4	0.02
KCl	0.02
KNO_3	0.02
"Mineral solution"	1 drop

from 1 June to 1 Dec. we found 165.5 mgrs. of dry bacterial substance, corresponding with ca. 83 mgrs. of permanganate per litre. As we see, the differences are considerable.

When a little natrium acetate was added to the anorganic solution, and when using a pure culture for inoculation, we could neither state an augmenting nor a diminishing of growth.

Thus we obtained in:

Distilled water	100
KCl	0.02
KNO_3	0.1
Natriumacetate	0.02
K_2HPO_4	0.02
"Mineral solution"	1 drop

by means of weighing, 220 mgrs. of dry bacterial substance per litre, corresponding with 110 mgrs. of permanganate, which figures are not exceedingly high and might likewise have been produced in the same time (4 months) from the air alone, without acetate.

In all these experiments with distilled water, the free surface of the liquid was also 80 cM², and the air had to pass through a dense cotton plug, with which the ERLÉNMEYER-flasks were closed. Already before we drew attention to the importance of the way in which the flasks are closed; be here still mentioned that we made some special experiments, which proved that a very narrow opening of the flasks, slackens the growth of *B. oligocarboophilus*, so that years may go by before the film has vigorously developed. We could not, however, expected anything else, for the considerable volume of air, required for the growth of the said quantities of bacteria, can only very slowly diffuse inward and outward through the narrow canal.

6. CARBONIC ACID CANNOT SERVE AS FOOD.

Various experiments were made to establish what may be the volatile atmospheric carbon compound which renders the growth of *B. oligocarbohilus* possible. That it cannot be carbonic acid, whether free or combined, resulted from the following experiments. In closed culture-flasks with the best nutrient solutions, and arranged in such a way, that at times a little free carbonic acid mixed with pure air, could artificially be introduced, it was not possible to get any growth. This experiment, which seemed of particular interest, has been so frequently repeated, and so long continued under different conditions, that we consider it as quite certain, that free carbonic acid cannot serve for the nutrition of *B. oligocarbohilus*.

For testing the influence of combined carbonic acid, cultures were made, firstly in the following solution:

Tap-water	100
Dikaliumphosphate	0.01
Kaliumnitrate	0.01
Natriumbicarbonate	0.1

When cultivating at the free air surely a luxurious growth was obtained, but it was by no means more vigorous than when the bicarbonate was left out.

If in this liquid the nitrate was replaced by an ammonium salt, the result was quite the same.

Secondly, the bicarbonate was replaced by common natrium carbonate, the same quantities of the different salts being used. But in this case the action proved rather injurious than favorable. It is true that the film had become considerable after a few months, but it was directly to be seen that the growth was so much inferior to that of cultures obtained in the same circumstances but in absence of carbonate, that the determination of the permanganate number seemed superfluous. Here, too, the replacing of nitrate by an ammonium salt or by a nitrite caused no change.

As a remarkable fact it may be mentioned, that in these experiments, in our large flasks, containing a litre of air, the thin bacterial film mounted very high up the dry glass-wall, which is likewise often observed in the solutions made with distilled water, and may repose on the absence of dissolved lime salts.

If the tap-water was substituted by distilled water, the addition of natrium carbonate did not cause an increase of bacterial growth either. We found, for instance, in:

Distilled water	100
K_2HPO_4	0.02
$(NH_4)_2SO_4$	0.02
Na_2CO_3	0.1
"Mineral solution"	1 drop

after 7 months (5 May—1 Dec.) 155 mgrs. of permanganate, corresponding with ca. 300 mgrs. of dry bacterial substance per litre, which production is less than that, obtained in other cases under the same circumstances but without carbonate, so that here also, the action of the carbonate, the long time of cultivation being taken into consideration, was not favorable. Quantities of carbonate, smaller than 0.1 %, were neither successful.

The results of this examination can be thus summarised, that for the growth of *B. oligocarbophilus* an atmospheric carbon compound is actually consumed, but that this cannot possibly be free carbonic acid. Furthermore, that also combined carbonic acid cannot serve for its nutrition.

7. NATURE OF THE ASSIMILATED ATMOSPHERIC CARBON COMPOUND.

If the carbonic acid of the air cannot be the food of *B. oligocarbophilus*, what other atmospheric carbon source might then come into consideration?

It is clear, that we should think here of the carbon-containing component of the air, discovered in 1862 by the botanist HERMANN KARSTEN ¹⁾, and recently discovered anew by French experimenters, especially by Mr. HENRIET ²⁾. It is true that the chemical nature of this substance has been hitherto unknown ³⁾, but yet it is certain that we have here to do with an easily oxidisable compound (or compounds), for a prolonged contact with alkali and air will already suffice to split off carbonic acid from it. Furthermore, according to the statement of the French investigator, the substance probably contains nitrogen.

This latter circumstance gives rise to the question whether this

¹⁾ H. KARSTEN. Zur Kenntniss des Verwesungsprocesses. Poggendorff's Annalen Bd. 191, pag. 343. 1862. To this place, as also to the not unimportant older literature on the carbon compound of the air, my attention was drawn by Mr. G. VAN ITERSOM.

²⁾ Comptes Rendus T. 135, pag. 89 et 101. 1902.

³⁾ HENRIET thinks that the substance must be a monosubstituted formamid with the formula $HCO.NHR$, where R represents a still unknown alkylrest. But then it is not easy to understand, why the production of carbonic acid takes place so readily. It might then rather be expected that, with an alkali a formiate would result and no carbonate.

nitrogen, like the carbon, is fit for assimilation by our microbe. Though this question has already partly been answered in the negative by the preceding experiments, it should still be remarked here that in nutrient liquids, without an expressly added nitrogen compound, for instance in:

Distilled water	100
K_2HPO_4	0.02
Mg, S, Mn, Fe	traces.

Or still better in:

Tap-water	100
K_2HPO_4	0.02

without any further addition, a not inconsiderable growth of *B. oligo-carbophilus* may occur, so that at least traces of an assimilable nitrogen compound may be drawn from the air by this bacterium, whereas, for the possibility of assimilation of the free atmospheric nitrogen no indications were found.

We now turn to another question, which the assimilation of the atmospheric carbon gives rise to, namely: How great is the quantity of the volatile substance wanted for the formation of the bacterial film produced in our cultures? This question is closely connected with the following: How much of the compound is moreover consumed by the respiration of our bacterium, escaping as free carbonic acid? For answering these questions we have to measure the quantity of the carbonic acid corresponding with a determined weight of dry bacterial substance, granted that the carbon percentage of this substance be known.

Our experiments relating to the measurement of the quantity of carbonic acid produced, are not yet closed, but as to the first part of the question, we give the following calculation to fix the volume of air wanted for the production of the carbon, actually accumulated in the bacterial films. We hereby make two chemical suppositions which, to be sure, are fairly well in accordance with truth. First, we admit that the carbon, freed from the unknown compound, as carbonic acid by a prolonged contact with alkali, is consumed quantitatively by our bacterium and, secondly, that the bulk of the bacterial cells consists of a substance possessing nearly the composition of cellulose¹⁾.

1) If accepting that the composition of the bacterial cells corresponds with that of albuminous substances, then, instead of 44% C., 52 to 55% C. should be brought into account, and in this proportion the volume of the air should be augmented.

Let us now consider the case when, in $\frac{1}{2}$ litre-flask with 100 cm^3 of fluid and a free surface of 80 cm^2 , after a month's culture a quantity of 20 mgrs. of dry bacterial substance is formed, which, calculated as cellulose, contains 44 % C.; we then find in the 20 mgrs. of dry matter 8.8 mgrs. of carbon. According to HENRIET the atmospheric carbon compound, present in a certain quantity of air, under prolonged action of alkali, gives out as much carbonic acid as occurs already in a free state in the same volume of air, that is per litre $0.3 \text{ cm}^3 = 0.6 \text{ mgrs.}$, in which 0.163 mgrs. of carbon are present. Thus, for 8.8 mgrs. are wanted 55 litres of air. Consequently, in the course of a month these 55 litres of air must have diffused through the cotton plug inward and outward of our $\frac{1}{2}$ litre-flasks, in order to produce the found quantity of carbon, that is 76 cm^3 hourly.

Though this figure should not be considered a priori as impossible, it still appears to be very high, and the difficulty of accepting it increases, if still the addition has to be made of a yet unknown, but apparently considerable amount consumed for the bacterial respiration, which, as remarked above, seems necessary. We therefore think that it must be admitted that the quantity of the atmospheric compound (or compounds) assimilable by *B. oligocarbophilus*, is much larger in our laboratory atmosphere, than in that of the Paris boulevard, analysed by HENRIET, and that we have here to do, with an extremely variable factor. The circumstance, too, that we have not as yet been able in our greenhouse, where the air, in the common sense of the word, is surely much purer than in the laboratory, to obtain a vigorous growth of *B. oligocarbophilus* pleads for this view. But here we could not always keep the temperature high enough, so that we consider our experiments in this direction not yet closed. Besides, we should observe, that in an empty, isolated room of the laboratory, the quantities of combined carbon drawn from the air, were as great, or only little less than in the laboratory itself, where the air was certainly impurer.

We are accordingly conscious that further experiments, with fresh atmospheric air are wanted to decide, whether the carbon compound occurs in the atmosphere in a constant or in a varying percentage. Only thereby it will be possible to ascertain the distribution of this compound, by which, at the same time, the signification of *B. oligocarbophilus* in nature will become clearer.

As to this signification, the question arises whether our microbe in substrata containing sufficient mineral nutrients (N, P, K, Mg, S, Fe, Mn), but being poor in organic substances, is able to build up the latter in the dark from the volatile carbon compounds occurring in the

atmosphere of the surrounding medium. And furthermore, whether carbon nutrition takes place exclusively in the floating dry films, — hence, in the earth, only on the relatively dry surface of the earth particles, — or that also in the depth of fluids growth and carbon assimilation be possible. The hitherto gathered experience about the self-purification of rivers and the biological purification of water in general, seems to exclude the latter hypothesis, and our own experiments too, render it not probable. The result of these experiments consists, in our opinion, in the very discovery of a microbe, which, in consequence of the film-formation, has the specific faculty, to absorb for its nutrition and multiplication, from a gas, namely the air, traces of volatile carbon compounds, by which the struggle for existence with the rest of the microbial world can be successfully sustained. The biological purification of water would, according to this view, find a counterpart in the biological purification of the air by *Bacillus oligocarbophilus*

Physics. — “The calculation of $\frac{e}{m}$ from the magnetic rotation of the plane of polarisation, for substances without an absorption band in the visible spectrum.” By Dr. L. H. SIERTSEMA. (Communication No. 82 from the Physical Laboratory at Leiden by Prof. H. KAMERLINGH ONNES).

Starting from FITZGERALD's ¹⁾ simple explanation of the magnetic rotation of the plane of polarisation derived from the ZEEMAN effect, and also from the supposition that the result of the magnetic force is only shown by the displacement of the dispersion curve of the medium ($n=f(\lambda)$) over a distance δ , HALLO ²⁾ finds for the magnetic rotation ω

$$\omega = -\frac{2\pi}{\lambda} z \delta \frac{dn}{d\lambda},$$

where z represents the thickness of the medium. HALLO's investigations are concerned with the parts of the spectrum in the neighbourhood of an absorption band and for these we are justified in making the above supposition, as appears from a formula derived by VOIGT

¹⁾ FITZGERALD. Proc. Roy. Soc. 63 p. 31.

²⁾ HALLO. Diss. Amsterdam 1902, p. 7.

from a more rigorous theory¹⁾. If, however we want to apply it to points at a greater distance from an absorption band, as is the case with the magnetic rotation of transparent substances, we must turn to VOIGT's more general formula²⁾

$$n = 1 + \Sigma \frac{\epsilon_h \mathfrak{D}^2 (\mathfrak{D}^2 - \mathfrak{D}_h^{0^2} \pm c_h R \mathfrak{D})}{(\mathfrak{D}^2 - \mathfrak{D}_h^{0^2} \pm c_h R \mathfrak{D})^2 + \mathfrak{D}_h^{1^2} \mathfrak{D}^2}.$$

If we may assume that only one term occurs under the summation in the second member, and also that $c_h R$ and $\mathfrak{D}_h^{1^2}$ are small compared with \mathfrak{D} , a simple reduction shows that the new dispersion curve may be derived from the original one by moving each point over a distance $\frac{1}{2} c_h R \frac{\mathfrak{D}^2}{\mathfrak{D}_h^{0^2}}$, which depends on \mathfrak{D} and hence also on the wave-length. In this case HALLO's relation will hold, if δ is not supposed constant, but proportional to λ^2 .

Though it is uncertain whether for a given transparent substance we are entitled to accept the formula for n with only one term under the summation, we may investigate to what results this would lead. From the elementary theory of the ZEEMAN effect it follows that

$$T^1 - T = \frac{e}{m} \frac{HT^2}{4\pi},$$

whence for the displacement of the dispersion curve

$$\delta = \lambda^1 - \lambda = \frac{e}{m} \frac{HT^2 V}{4\pi} = \frac{e}{m} \frac{H\lambda^2}{4\pi V}.$$

This value has been derived for the absorption band. From the above considerations it follows, however, that we may apply it for each wave-length, and hence we find

$$\omega = \frac{2\pi}{\lambda} z \frac{e}{m} H \frac{\lambda^2}{4\pi V} \frac{dn}{d\lambda} = z H \frac{e}{m} \frac{\lambda}{2V} \frac{dn}{d\lambda}.$$

Whence follows for the rotation constant $\varrho = \frac{\omega}{zH}$:

$$\varrho = \frac{e}{m} \frac{\lambda}{2V} \frac{dn}{d\lambda},$$

which formula corresponds with one, given by VOIGT³⁾, if we replace the k occurring there by:

$$k = \frac{e}{m} \frac{1}{2} V,$$

¹⁾ VOIGT. Wied. Ann. 67 p. 351.

²⁾ VOIGT. Wied. Ann. 67 p. 349.

³⁾ VOIGT. Wied. Ann. 67 p. 351.

which value may also be derived directly, if we equate the magnetic displacement $\frac{1}{2} c_h R$ after VOIGT with that resulting from the elementary theory. The dispersion of the magnetic rotation expressed by this formula is the same as that resulting from BECQUEREL's ¹⁾ relation and found by him to be confirmed in the case of carbon disulphide and creosote.

The relation found for ϱ enables us to compute $\frac{e}{m}$ as soon as we know the rotation constant ϱ and the dispersion $\frac{dn}{d\lambda}$ of a substance for the same wavelength λ . For we have

$$\frac{e}{m} = \frac{2V}{\lambda} \varrho \frac{d\lambda}{dn}.$$

We shall make the calculation for some substances at a value of $\lambda = 589 \mu\mu$. The rotation constants r being usually expressed in minutes we have

$$\varrho = r \frac{2\pi}{360 \times 60}$$

and hence we find

$$\frac{e}{m} = \frac{2 \times 3 \times 10^{10}}{589} \frac{2\pi}{360 \times 60} \times r \frac{d\lambda}{dn} = 2.96 \times 10^4 \times r \frac{d\lambda}{dn}.$$

1. *Air* (100 KG., 13°.0). I have found ²⁾ $r = 553.10^{-6}$. PERREAU ³⁾ finds for the refractive index at (1 atm., 0° C.)

$$\lambda = 644, \quad n - n_D = \frac{85.10^{-8}}{538} \quad \frac{88.10^{-8}}{538}$$

whence $\frac{d\lambda}{dn} = 0.65 \times 10^8$ and 0.58×10^8 , on an average 0.61×10^8 .

Supposing $n-1$ proportional to the density, it follows that for air (100 kilogram, 13°.0 C.) $d\lambda/dn = 0.648 \times 10^8$ and we find:

$$\frac{e}{m} = 2.96 \times 553 \times 0.648 \times 10^4 = 1.06 \times 10^7.$$

In the same way is found for:

2. *Carbon dioxide* (1 atm. 6°.5). $r = 8.62 \times 10^{-6}$

$$\frac{d\lambda}{dn} (1 \text{ atm., } 0^\circ) = 3.42 \times 10^7$$

$$(1 \text{ atm., } 6^\circ.5) = 3.50 \times 10^7$$

¹⁾ BECQUEREL. C. R. 125 p. 679.

²⁾ SIERTSEMA. Comm. Lab. Leiden. Suppl. N°. 1, p. 86; Arch. Néerl. (2) 2 p. 376.

³⁾ PERREAU. Ann. de Ch. et de Ph. (7) 7 p. 289.

$$\frac{e}{m} = 0.89 \times 10^7.$$

3. *Hydrogen* (85.0 Kilogram, 9°.5 C.) $r = 456 \times 10^{-6}$
 $d\lambda/dn$ (1 atm., 0° C.) $= 10^8$
 (85.0 KG., 9°.5 C.) $= 1.31 \times 10^6$,

$$\frac{e}{m} = 1.77 \times 10^7.$$

4. *Water*. From refractive indices of DUFET ¹⁾ and the magnetic rotation constant 0.0130 we get

$$\frac{e}{m} = 1.25 \times 10^7.$$

5. *Carbon disulphide*. In the same way with $r = 0.042$ we find from VAN DER WILLIGEN's ²⁾ refractive indices

$$\frac{e}{m} = 0.745 \times 10^7.$$

6. *Quartz*. $r = 0.01684$ ³⁾. By means of VAN DER WILLIGEN's refractive indices we find

$$\frac{e}{m} = 1.25 \times 10^7.$$

It may be remarked that the values of $\frac{e}{m}$ found here correspond in order of magnitude with those found in other ways.

¹⁾ DUFET. Bull. Soc. Minér. 8 p. 218.

²⁾ V. D. WILLIGEN. Arch. Mus. Teyler III. 1. p. 55.

³⁾ BOREL, C. R. 128, p. 1095.

KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN
TE AMSTERDAM.

PROCEEDINGS OF THE MEETING

of Saturday January 31, 1903.

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D. J. KORTEWEG: "Plaitpoints and corresponding plaitis in the neighbourhood of the sides of the ψ -surface of VAN DER WAALS", p. 445. (With one plate).

A. H. SIRKS: "Some remarkable phenomena, concerning the electric circuit in electrolytes". (Communicated by Prof. H. A. LORENTZ), p. 465.

The following papers were read:

Chemistry. — "*The velocity of transformation of Carbon monoxide.*"

By Dr. A. SMITS and L. K. WOLFF. (Communicated by Prof.
H. W. BAKHUIS ROOZEBOOM).

(Communicated in the meeting of December 27, 1902).

From the researches of BOUDOUARD¹⁾ on the equilibrium $2\text{CO} \rightleftharpoons \text{CO}_2 + \text{C}$, where use was made of the accelerating action of the metals Ni, Co, Fe, it follows that they do not modify the equilibrium but only

¹⁾ Ann. de Chimie et de Physique [7] 24, p. 5 (1901).

exercise an influence on the velocity and are, therefore, catalyzers. It was shown by BOUDOUARD that, whilst CO_2 in contact with C is practically totally converted at 1000° into CO, the amount of CO_2 in the gaseous mixture in equilibrium increases at lower temperatures in accordance with the sign of the heat effect $\text{CO}_2 + \text{C} = 2\text{CO} - 42000$ cal. until at 445° the CO is practically completely converted into CO_2 and C.

From this follows that below 445° , CO exists in a *metastable* condition.

INVESTIGATION.

a. Preparation of the catalyzer and preliminary experiments.

1. The following research was instituted with the object of determining velocities of reaction in the metastable region in presence of a catalyzer. The apparatus employed by us was in the main the same as that used by VAN 'T HOFF in his research on the velocity of transformation of detonating gas into water. The reaction vessel, however, was filled with a catalyzer obtained in the following manner.

Pumice stone was broken up into small lumps, drenched with a solution of $\text{Ni}(\text{NO}_3)_2$ then dried, ignited and finally reduced in a current of hydrogen or carbon monoxide.

This reduction, it was observed, takes place in two stages. The greyish-black surface of NiO first turns yellow owing to the formation of a suboxide (Ni_2O_3)¹⁾ and afterwards on complete reduction again becomes dark-grey. When operating at a high temperature, reduction with H_2 or CO gives apparently, the same material. If, however, the reduction takes place in a current of CO at 445° a layer of carbon is deposited on the reduced nickel.

2. The experiments with nickel-pumice obtained by reduction with either H_2 or CO at a *high* temperature gave the following result²⁾.

At 310° (boiling point of diphenylamine) the activity of the catalyzer did not appear constant. Successive fillings continually gave smaller diminutions of pressure in the same length of time.

¹⁾ MÜLLER, Bell (Chemical News 20, 258).

²⁾ Coating the inner wall of the reaction vessel with nickel did not appear to affect the result, probably because the surface of the glass wall was very small as compared with the surface of the catalyzer.

We found for instance :

310°.

Filling.	Diminution in mM. Hg. during 10 minutes.
1st	5,68
2nd	5,00
3rd	3,80

ect.

As we suspected that the retrogression of the activity of the catalyzer was due to the ever increasing layer of C, which deposits on the catalyzer during the experiment and fillings, we next used a nickel-pumice which had been reduced at 445° and was in consequence already coated with a layer of carbon. Although at first there was still a perceptible diminution in the activity, the differences in successive fillings become gradually smaller and finally, the activity was constant as seen from the following table:

310°

Filling.	Diminution in mM. Hg. during 10 minutes.
1st	1,88
2nd	1,80
3rd	1,78
4th	1,74
5th	1,75
6th	1,74
7th	1,74

Being satisfied with this result, we started our investigation with the catalyzer of constant activity obtained in this way.

b. Measurements concerning the order of the reaction.

For the determination of the order of the reaction the method of VAN 'T HOFF was first of all applied. It is given in this case by the equation:

$$n = \frac{\log \left(\frac{dc_1}{dt} : \frac{dc_2}{dt} \right)}{\log (c_1 : c_2)}$$

The determination was made at 310°.

In the first experiment the pressure of the CO was 786,8 mm. Hg at the commencement; after 30 minutes the pressure amounted to 739,9 mm. Hg. The diminution of pressure in 30 minutes therefore amounted to 46,9 mm. Hg.

If we take for $\frac{dc}{dt}$ the diminution of pressure per minute then $\frac{dc_1}{dt}$ becomes 1,56.

In the second experiment the pressure of the CO was 535,3 mm. Hg at the commencement and after 30 minutes the pressure had come down to 501,7 mm. Hg. Here, the diminution of pressure in 30 minutes amounted, therefore, to 33,6 mm. Hg or $\frac{dc_2}{dt} = 1,12$.

C_1 = aver. of press. at beginn. and end at the 1st experim. = 763,35 mm. Hg.

C_2 = " " " " " " " " " " 2nd " = 518,5 " "

If from this we calculate n , we find

$$n = 0,86,$$

from which it is apparent that the reaction is a monomolecular one. In order to make more certain of this, the order of the reaction was also determined at two other temperatures according to the method given by NOYES. In this case n is calculated from the following formula:

$$n = 1 + \frac{\log \frac{t_1}{t_2}}{\log \frac{c_2}{c_1}}.$$

in which t_1 and t_2 are the times during which the same part of the original quantity is converted when starting from different concentrations c_1 and c_2 .

At 256° we obtained the following result:

$$n = 1 + \frac{\log \frac{192}{200}}{\log \frac{525,1}{770,9}} = 1,1.$$

The experiment at 340° gave

$$n = 1 + \frac{\log \frac{60}{58}}{\log \frac{519,0}{792,8}} = 0,92.$$

The observations at the three temperatures 256°, 310° and 340°, therefore lead to the conclusion that we are really dealing here with a *monomolecular* reaction.

c. Determination of the reaction-constant at 256°, 310°, 340°.

These determinations were conducted with the same reaction vessel and the same catalyzer.

256° (boiling point of amyl benzoate).

Time in minutes.		Pressure in m.m. Hg	$k = \frac{1}{t} \log \frac{P_0}{2P_t - P_0}$
1	2		
0		761.0	—
5	0	758.9	0.000464
10		757.6	0.000381
	10	756.4	0.000287
	20	754.1	0.000276
	30	751.7	0.000277
	40	749.3	0.000278

average 0.000279

The following may serve to elucidate this table:

At 256° the catalyzer seemed to still perceptibly absorb the CO, which caused the diminution of pressure during the first 5 minutes to be excessive. The values for k are, therefore, not constant when we start from the pressure corresponding with the time 0, but they gradually diminish which may be seen from the first two figures in the last column of the table. To eliminate the error caused by absorption, we have, when calculating k , started from the pressure corresponding with the time 5 minutes (column 2) and, therefore, have called this pressure P_0 . As the CO concentration had diminished very little in 5 minutes the error thus introduced could be disregarded. The values obtained for k are found in the last column beneath the dotted line. The following table relates to the temperature 310°.

310° (boiling point of diphenylamine)

Time in minutes	Pressure in m.m. Hg	$k = \frac{1}{t} \log \frac{P_0}{2P_t - P_0}$
0	786.8	
10	769.8	0.00192
20	754.8	0.00184
30	739.9	0.00184
40	725.6	0.00184

average 0.00186

As was to be expected, the absorption at this high temperature was scarcely perceptible and in the following table, which shows the results obtained at 340°, no absorption whatever was noticed.

340° (boiling point of phenantrene)

Time in minutes	Pressure in m.m. Hg	$k = \frac{1}{t} \log \frac{P_0}{2P_t - P_0}$
0	791.4	
10	746.4	0.00524
20	705.9	0.00527
30	668.7	0.00536
50	642.7	0.00521

average 0.00527

In order to make sure that the activity of the catalyzer had not diminished during these three series, a series of experiments was finally taken at 310° with the following result.

310°

Time in minutes	Pressure in m.m. Hg	$k = \frac{1}{t} \log \frac{P_0}{2P_t - P_0}$
0	895.5	
10	788.3	0.00189
20	773.0	0.00183
30	757.8	0.00182
40	742.8	0.00184

average 0.00184

The activity of the catalyzer had, therefore, undergone no change during these measurements, so that we were justified in calculating the temperature-coefficient from the results obtained. The result was as follows:

Temperature.	k .	$\frac{k_{t+10}}{k_t}$
256°	0.000279	$> 1,4$
310°	0.00186	$> 1,4$
340°	0.00527	

d. Mechanism of the reaction.

What idea are we to form about the mechanism of the reaction if this takes a monomolecular course?

If we assume the formation of $\text{Ni}(\text{CO})_4$ with an immeasurably large velocity and the subsequent breaking up of this compound according to the equation



we must also accept the equilibrium



of which the constant is given by the equation:

$$K = \frac{C_{\text{co}}^4}{C_{\text{Ni}(\text{co})_4}}$$

This would then necessarily lead to the conclusion, that the velocity

of reaction should be proportional to the 4th power of the CO-concentration whereas it appears to be proportional to the 1st power of the CO-concentration. Rejecting this hypothesis two further suppositions remain.

Firstly :



Secondly :



In the last case it need not be assumed that one of these reactions takes place with unmeasurable velocity, but only that the second one proceeds more rapidly than the first.

As regards the nature of the catalyzer we think we may conclude from the result of several experiments, that it is not the carbon but the finely divided nickel which possesses the catalytic action.

Amsterdam, Chem. Lab. University. Dec. 1902.

Chemistry. — Professor BAKHUIS ROOZEBOOM presents a communication from Dr. J. J. VAN LAAR on: "*The course of the melting-point-lines of solid alloys or amalgams.*" (First Communication). (Communicated in the meeting of December 27, 1902).

1. In the researches of VAN HETEREN¹⁾ on Tinamalgams a meltingpoint-line occurs²⁾ of a kind, which has not as yet been studied over such an extended course (from 0 to nearly 100 atom % of mercury). This is chiefly due to the fact, that the temperatures of fusion of the two metals are so very different; tin 231°, mercury —38.6°. In consequence the meltingpoint-line of the tin meets that of the mercury

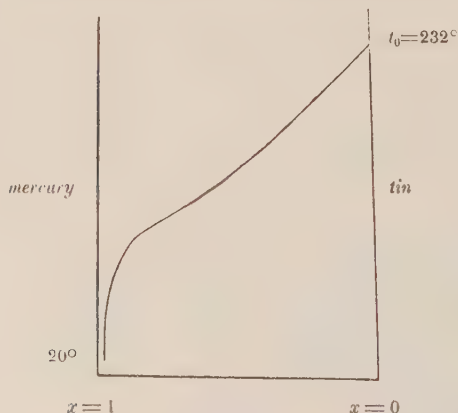


Fig. 1.

practically at 100 atom % mercury, so that the meltingpoint-line of the mercury has not even been observed. We therefore see for the first time a meltingpoint-line in its full course, and the question arises whether the course, found by VAN HETEREN, may be predicted theoretically.

The answer to this is in the affirmative. Let us, to start with, take the most simple view as regards the molecular poten-

¹⁾ Dissertation 1902. (also Report Meeting 29 Nov. 1902).

²⁾ l. c. pg. 18.

tials μ of the tin as solid substance and μ_1 of the tin in the liquid amalgam, namely that

$$\left. \begin{aligned} \mu &= e - c T \\ \mu_1 &= e_1 - c_1 T + RT \log (1-x) \end{aligned} \right\} \cdot \cdot \cdot \cdot \cdot (1)$$

In this it has been assumed, firstly that the tin, crystallised from the amalgam, does not consist of mixed crystals, but of pure tin — a supposition, which has been proved by experiment to be nearly correct — and secondly, that the energy-quantity e is no function of x . Later on we will drop this last simplified supposition, and demonstrate, that a more accurate calculation of the function μ_1 affects the course of the meltingpoint-lines *quantitatively*, but not *qualitatively*. Then it is our object to demonstrate at once, that the entire qualitative course, as represented in the figure, follows from the equations (1) in connection with the *course of the logarithmic function of $1-x$* . By putting the two potentials equal to each other, we obtain:

$$(e_1 - e) - (c_1 - c) T = - RT \log (1-x),$$

or calling $e_1 - e = q$ (the heat of fusion of the solid tin, when passing into the amalgam), and the quantity $c_1 - c = \gamma$:

$$q - \gamma T = - RT \log (1-x),$$

from which follows:

$$T = \frac{q}{\gamma - R \log (1-x)} \cdot \cdot \cdot \cdot \cdot (2)$$

This is then the most simple form of the meltingpoint-line.

On introducing the temperature of fusion of pure tin T_0 , x becomes 0, and we obtain:

$$T_0 = \frac{q}{\gamma},$$

so that we may also write:

$$T = \frac{T_0}{1 - \frac{RT_0}{q} \log (1-x)} = \frac{T_0}{1 - \theta \log (1-x)}, \cdot \cdot \cdot \cdot \cdot (3)$$

if we abbreviate $\frac{RT_0}{q}$ to θ .

We notice at once, that on the development of the logarithmic function, the formula, for very small values of x , passes into

$$T = \frac{T_0}{1 + \frac{RT_0}{q} x},$$

that is to say into
$$T_0 - T = \frac{RT_0}{q} x,$$

the ordinary formula of VAN 'T HOFF for extremely dilute solutions. If, however, the solutions are no longer extremely dilute, we can no longer be satisfied with one or two terms in the development of $\log(1-x)$, but $\log(1-x)$ must remain.

I will now show, that the approximative relation

$$T = \frac{T_0}{1 - \theta \log(1-x)}$$

gives indeed the observed course qualitatively. For $\frac{dT}{dx}$ we find:

$$\frac{dT}{dx} = - \frac{T_0}{(1 - \theta \log(1-x))^2} \cdot \frac{\theta}{1-x}.$$

Whilst T itself, for $x=0$, passes into T_0 , and for $x=1$ into $T=\infty$, which already agrees with the steadily declining course — it appears from $\frac{dT}{dx}$, that this quantity, for $x=0$, becomes:

$$\left(\frac{dT}{dx}\right)_0 = - T_0 \theta = - \frac{RT_0^2}{q},$$

the limiting value of VAN 'T HOFF, whilst for $x=1$ it passes into $-\infty$. It may now still be asked, whether there will be a point of inflection or not. In the case, examined by VAN HETEREN, a point of inflection plainly occurred at about $x=0.8$, but it may also be possible, that the course was like the one in the following figure, without point of inflection. Let us therefore determine

$$\frac{d^2T}{dx^2}.$$

Fig. 2.

$$\frac{d^2T}{dx^2} = \frac{2 T_0}{(1 - \theta \log(1-x))^3} \cdot \frac{\theta^2}{(1-x)^2} - \frac{T_0}{N^2} \cdot \frac{\theta}{(1-x)^2} = \frac{T_0}{N^2} \cdot \frac{\theta}{(1-x)^2} \left[\frac{2\theta}{N} - 1 \right].$$

Evidently $\frac{d^2T}{dx^2} = 0$, when $2\theta = N$, that is to say, when

$$\begin{aligned} 1 - \theta \log(1-x) &= 2\theta \\ -\log(1-x) &= 2 - \frac{1}{\theta}. \end{aligned}$$

As $\theta = \frac{RT_0}{q}$ will be positive, we see, that the point of inflection can

only occur if θ is situated between $\frac{1}{2}$ and ∞ . For $\theta = \frac{1}{2}$, $x = 0$; for $\theta = \infty$ we find on the other hand $x = 0.865$. A point of inflection further than $x = 0.865$ can only occur with negative values for θ ($\theta = -\infty$ till $\theta = 0$, when $x = 0.865$ till $x = 1$). But there is no point of inflection if $\theta < \frac{1}{2}$, that is to say, if

$$q > 2 R T_0,$$

or in gram-cals.

$$q > 4 T_0.$$

In our case therefore, where $T_0 = 505$ — when $q > 2000$ gram-cals.

This last conclusion will however be modified, when we apply the necessary correction to the approximate formula (3). *But the fact of the possible occurrence of a point of inflection* may already be completely explained by the simple formula (3), and this by the course of the function $\log (1-x)$.

II. We now proceed to write down a more stringent relation than (3).

Assuming an equation of condition of the VAN DER WAALS's kind, the value of μ_1 (the molecular potential of the component n_1) becomes as follows:

$$\begin{aligned} \mu_1 = & -k_1 T (\log T - 1) - RT (\log (V-b) - 1) + \left((e_1)_0 - T (n_1)_0 \right) + \\ & + \frac{\sum n_1 \cdot RT}{V-b} b_1 - \frac{2}{V} (n_1 a_{11} + n_2 a_{12} + \dots) + RT \log n_1 \quad \dots \quad (4) \end{aligned}$$

For b has been written:

$$b = n_1 b_1 + n_2 b_2 + \dots,$$

whilst for a the quadratic relation

$$a = n_1^2 a_{11} + 2 n_1 n_2 a_{12} + \dots$$

has been taken.

Now, $\log (V-b)$ can be supposed to be independent of x , whilst the expression

$$\frac{\sum n_1 \cdot RT}{V-b} b_1 - \frac{2}{V} (n_1 a_{11} + n_2 a_{12}) = \frac{RT}{V-b} b_1 - \frac{2}{V} ((1-x)a_{11} + xa_{12})$$

in regard to x will become not of the order x , but of x^2 . Let us, to prove this, rather start from a more general expression for the total potential ζ (in our case we have only to deal with two single components n_1 and n_2), namely

$$\begin{aligned} \zeta = & n_1 (\mu_1)_0 + n_2 (\mu_2)_0 + \frac{n_1^2 \mu_{11} + 2n_1 n_2 \mu_{12} + n_2^2 \mu_{22}}{n_1 + n_2} + \\ & + RT \left(n_1 \log \frac{n_1}{n_1 + n_2} + n_2 \log \frac{n_2}{n_1 + n_2} \right). \end{aligned}$$

We then find:

$$\mu_1 = \frac{\partial \xi}{\partial n_1} = (\mu_1)_0 - \frac{1}{(n_1 + n_2)^2} (n_1^2 \mu_{11} + 2 n_1 n_2 \mu_{12} + n_2^2 \mu_{22}) + \\ + \frac{2}{n_1 + n_2} (n_1 \mu_{11} + n_2 \mu_{12}) + R T \log \frac{n_1}{n_1 + n_2}.$$

With $n_1 + n_2 = 1$, $n_1 = 1 - x$, $n_2 = x$ we obtain:

$$\mu_1 = (\mu_1)_0 - [(1-x)^2 \mu_{11} + 2x(1-x)\mu_{12} + x^2 \mu_{22}] + 2[(1-x)\mu_{11} + x\mu_{12}] + R T \log(1-x),$$

or after simplification:

$$\mu_1 = [(\mu_1)_0 + \mu_{11}] - x^2 (\mu_{11} - 2 \mu_{12} + \mu_{22}) + R T \log (1 - x).$$

In analogy with (4) we may therefore write:

$$\mu_1 = e_1 - c_1 T + \alpha_1 x^2 + R T \log (1 - x).$$

The terms with $T \log T$ have not been taken into consideration, because they disappear on account of the equality of the quantities k_1 and R in the liquid and in the solid phase.

If, for the sake of a closer approximation, we take up some higher powers of x , we finally get:

$$\left. \begin{array}{l} \text{(solid tin)} \quad \mu = e - cT \\ \text{(tin in liquid amalg.)} \quad \mu_1 = e_1 - c_1 T + (\alpha_1 x^2 + \beta_1 x^3 + \gamma_1 x^4) + R T \log(1-x) \end{array} \right\} \quad (5)$$

Equating, we then find as in § 1:

$$q_0 - \gamma T = -(\alpha_1 x^2 + \beta_1 x^3 + \gamma_1 x^4) - R T \log (1 - x),$$

or

$$T = \frac{q_0 + (\alpha_1 x^2 + \beta_1 x^3 + \gamma_1 x^4)}{\gamma - R \log (1 - x)} \quad . \quad . \quad . \quad . \quad . \quad (6)$$

The heat of fusion of the solid tin in the amalgam is now plainly:

$$q = q_0 + (\alpha_1 x^2 + \beta_1 x^3 + \gamma_1 x^4). \quad . \quad . \quad . \quad . \quad . \quad (7)$$

For $x = 0$, (6) passes into

$$T_0 = \frac{q_0}{\gamma},$$

so we may again write:

$$T = T_0 \frac{1 + \frac{\alpha_1 x^2 + \beta_1 x^3 + \gamma_1 x^4}{q_0}}{1 - \frac{R T_0}{q_0} \log (1 - x)},$$

or with $\frac{\alpha_1}{q_0} = \alpha$, $\frac{\beta_1}{q_0} = \beta$, $\frac{\gamma_1}{q_0} = \gamma$:

$$T = T_0 \frac{1 + (\alpha x^2 + \beta x^3 + \gamma x^4)}{1 - \theta \log (1 - x)}, \quad . \quad . \quad . \quad . \quad . \quad (8)$$

and this is the more accurate formula, which has taken the place of the simple relation (3).

III. We will now show, that the above formula quantitatively yields the values, found by VAN HETEREN for T , in a satisfactory manner.

As $-\left(\frac{dT}{dx}\right)_0 = T_0 \theta$, θ may be determined with great accuracy from the beginning course of the meltingpoint-line. From the values, found for T (on pg. 16 of the dissertation) for $x = 0$ atom % of mercury (pure tin), $x = 0,1005$, $x = 0,1716$ and $x = 0,2338$, the average value, obtained for $-\frac{dT}{dx}$ is $= 200$. From the determinations of HEYCOCK and NEVILLE between $x = 0$ and $x = 0,1$ it also follows, that $-\frac{dT}{dx} = 200$.

For θ we may therefore take ($T_0 = 505$):

$$\theta = \frac{200}{505} = \underline{0,4}.$$

I calculated the values of α , β and γ as follows:

$$\underline{\alpha = 0,325} \quad ; \quad \underline{\beta = -1,11} \quad ; \quad \underline{\gamma = 1,33}.$$

Formula (8) thus becomes:

$$T = T_0 \frac{1 + (0,325x^2 - 1,11x^3 + 1,33x^4)}{1 - 0,4 \log(1-x)},$$

and so we find the following values for T .

The agreement is as good as can be expected: the difference between the calculated value of T and the observed value generally amounts to fractions of a degree, average $0,8$; as regards to the absolute temperatures the deviation is only average $0,2\%$. Only the two last values are too low (the last 3%), but then the influence of a small inaccuracy in the determination of the coefficients β and γ makes itself strongly felt. If we except these two last values, the calculated meltingpoint-line fully coincides with the observed line in the scale of the figure in the dissertation. And by means of a slight alteration in the value of β and γ we might perhaps cause the two last observations to agree. Let us not forget, that the formula (8) always remains an approximate one. In the last values of x the composition of the separated tin must also make its influence felt. For this is no longer pure tin but contains certainly 1% , or perhaps even 6% of mercury.

As regards the value of q (the heat of fusion of tin, when passing into the amalgam) — when $x = 0$, $q = q_0$, that is to say $= \frac{RT'_0}{\theta} = \frac{1010}{0,4} = 2550$ gram-cals. At 25° our formula is no longer available, as

x	x^2	x^3	x^4	$-\log(1-x)$	Numer.	Denom.	$T - 273$ calcul.	$T - 273$ found	Δ
0,1005	0,0101 ⁰	0,00101 ⁵	0,0001 ⁰²⁹	0,1059	1,0023	1,0424	212,4	214,6	0,8
0,1716	0,0294 ⁵	0,0050 ⁵³	0,0008 ⁶⁷³	0,1883	1,0054	1,0753	198,9	198,6	0,3
0,2338	0,0546 ⁶	0,0127 ⁸	0,0029 ⁸⁸	0,2663	1,0076	1,1065	186,7	183,7?	3,0?
0,2969	0,0881 ⁵	0,0261 ⁷	0,00777 ⁴	0,3523	1,0099	1,1409	173,8	173,0	0,8
0,3856	0,1487	0,0573 ³	0,0221 ¹	0,4872	1,0141	1,1949	155,4	155,2	0,2
0,5001	0,2501	0,1251	0,0625 ⁵	0,6933	1,0256	1,2773	132,3	133,4	-1,1
0,5973	0,3568	0,2131	0,1273	0,9095	1,0488	1,3638	115,2	115,2	0,0
0,6467	0,4182	0,2705	0,1749	1,0404	1,0682	1,4161	107,7	107,4	0,3
0,6754	0,4562	0,3081	0,2081	1,1252	1,0830	1,4501	104,0	103,4	0,6
0,6813	0,4642	0,3162	0,2155	1,1435	1,0866	1,4574	103,3	102,4	0,9
0,7104	0,5047	0,3585	0,2547	1,2393	1,1047	1,4957	99,8	99,0	0,8
0,7155	0,5119	0,3663	0,2620	1,2570	1,1083	1,5028	99,2	98,8	0,4
0,7477	0,5591	0,4180	0,3126	1,3772	1,1335	1,5509	95,9	95,4	0,5
0,7547	0,5696	0,4299	0,3244	1,4053	1,1393	1,5621	95,1	94,0	1,1
0,7963	0,6341	0,5049	0,4021	1,5912	1,1805	1,6365	91,1	90,0	1,1
0,8189	0,6706	0,5492	0,4497	1,7087	1,2064	1,6835	88,7	88,4	0,3
0,8921	0,7958	0,7100	0,6333	2,2266	1,3128	1,8906	77,5	79,7	-2,2
0,9483	0,8993	0,8528	0,8087	2,9623	1,4212	2,1849	55,3	65,2	-9,9

according to the above table it only yields trustworthy values for T up to about 90° . At 90° $x = 0,8$, and then, according to (7), we have:

$$q = q_0 [1 + (\alpha x^2 + \beta x^3 + \gamma x^4),$$

or

$$q = q_0 [1 + 0.325 x^2 - 1.11 x^3 + 1.33 x^4],$$

that is to say $q = 1.185 q_0 = 3020$ gram-cals.,

whilst VAN HETEREN (at 25°) found ± 3000 gram cals, by means of electromotive measurements ¹⁾. The concordance is absolute.

We, finally, wish to remark, that according to the determinations of VAN HETEREN and of HEYCOCK and NEVILLE, regarding the lowering of the temperature of fusion of tin on adding small quantities of mercury, q_0 must be $= 2550$ cals. We therefore see, that the value, assigned by PERSON, namely $14.25 \times 118.5 = 1690$ gram cals., is much too small. In a later communication I will show, that the heat of fusion of mercury, given by PERSON, is also many times too small.

Dec. 1902.

¹⁾ Dissertation pg. 49.

Chemistry. — “On the potential-difference, which occurs at the surface of contact of two different non-miscible liquids, in which a dissolved electrolyte has distributed itself.” By Dr. J. J. VAN LAAR. (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM.)

(Communicated in the meeting of December 27, 1902.)

1. It has already been demonstrated by NERNST¹⁾ in 1892, that a potential-difference must occur at the surface of contact of two liquids, which lie together in layers, such as for instance water and phenol, on account of the unequal distribution of the neutral molecules and the Ions of a dissolved electrolyte. It is true, that his expression for the electromotive force relates to the case, that one of the two phases is a *solid* solution, but it will be perceived at once, that the same formula also applies to our case²⁾.

There is, however, at present no prospect of obtaining direct measurements of this potential-difference³⁾. But as RIESENFELD⁴⁾ has lately been experimenting on the subject, although in another direction, it may be as well to give the exact theory of the phenomenon, which I worked out about a year ago, when engaged in writing a book on electro-chemistry, which will be published later.

Suppose we have a solution of KCl in the solvents A_1 and A_2 .

A_1		A_2	
KCl ₁	Cl	K	KCl ₂
	Cl	K	
	Cl	K	

If now equilibrium has been established between the *non-dissociated*, electrically neutral portions of the dissolved KCl in the two phases, there need not be equilibrium between the *Ions* in the two solvents. Indeed, equating the thermodynamic potentials for equivalent quantities of the non-dissociated portions in the two phases (*equilibrium of partition*), we get:

$$\mu_{KCl_1} = \mu_{KCl_2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

But the two dissociation-equilibria give:

$$\mu_{KCl_1} = \mu_{K_1} + \mu_{Cl_1} \quad ; \quad \mu_{KCl_2} = \mu_{K_2} + \mu_{Cl_2} \quad . \quad . \quad . \quad (2)$$

Consequently it will suffice if .

$$\mu_{K_1} + \mu_{Cl_1} = \mu_{K_2} + \mu_{Cl_2} \quad , \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

¹⁾ Zeitschr. für Physik. Chemie **9**, 137 (1892).

²⁾ Compare RIESENFELD, Wied. Ann. (4) **8**, 617 (1902).

³⁾ Ibid., l. c.

⁴⁾ NERNST und RIESENFELD, l. c. p. 600—608; RIESENFELD, 609—615; 616—624; id. Inaug. Diss., Göttingen 1901; HITTOFF, Wied. Ann. (4) **9**, 243—245 (1902).

and it would be a sheer accident if we also had:

$$\mu_{K_1} = \mu_{K_2} ; \mu_{Cl_1} = \mu_{Cl_2}.$$

There exists therefore as a rule *no* equilibrium of partition between the *Ions* in the two solvents. For example there may be in the second solvent relatively too few K-Ions, too many Cl-Ions. Since a system out of equilibrium tends to pass into a condition of equilibrium, K-Ions from A_1 will migrate to A_2 , and remain there in the boundary-layer, while the corresponding liberated Cl-Ions remain in the boundary-layer of A_1 (inversely Cl-Ions will migrate from A_2 to A_1 , whilst the corresponding liberated K-Ions remain in A_2 . Both add themselves to the above mentioned similar ions in the boundary-layer). The consequence is the occurrence of an *electrical doublelayer* and therefore of a potential-difference. And it is this potential-difference, which will restore the originally non-existing equilibrium between the Ions.

All this may be put into a very simple mathematical form.

Let V_1 be the electrical potential of A_1 , V_2 that of A_2 , so that $\Delta = V_2 - V_1$ represents the potential-difference at the boundary (in the case we are dealing with, Δ is therefore *positive*), then the formula for the equilibrium of the K-Ions will be:

$$\frac{\mu_{K_2} - \mu_{K_1}}{\epsilon} de + \Delta de = 0,$$

which is at once obvious, when we consider the virtual passage from the left to the right over the boundary of such a quantity of K-Ions, that the quantity of electricity transported is de . As the quantities μ relate to *equivalent*-quantities, and as these do not correspond with one electric unit, but with $\epsilon (= 96530)$ electric units, $\mu_{K_2} - \mu_{K_1}$ must be divided by ϵ .

For the equilibrium of the Cl-Ions we find in the same manner:

$$\frac{\mu_{Cl_2} - \mu_{Cl_1}}{\epsilon} - \Delta de = 0.$$

The sign at Δ is now negative, because on account of the negative charge the change in the electrical energy is $-\Delta de$.

We therefore obtain from the two relations, after dividing by de :

$$\Delta = - \frac{\mu_{K_2} - \mu_{K_1}}{\epsilon} = \frac{\mu_{Cl_2} - \mu_{Cl_1}}{\epsilon} (4)$$

That these two equations for Δ are not conflicting, is at once apparent. For the relation, resulting therefrom

$$\mu_{K_1} - \mu_{K_2} = \mu_{Cl_2} - \mu_{Cl_1},$$

leads at once to (3).

If we introduce:

$$\mu = \mu' + RT \log c,$$

in which c is the *concentration* of the Ions, we may also write:

$$\Delta = -\frac{1}{\varepsilon} \left[(\mu'_{K_2} - \mu'_{K_1}) + RT \log \frac{c_{K_2}}{c_{K_1}} \right] \left\{ \begin{array}{l} \dots \dots \dots (5) \\ \Delta = \frac{1}{\varepsilon} \left[(\mu'_{Cl_2} - \mu'_{Cl_1}) + RT \log \frac{c_{Cl_2}}{c_{Cl_1}} \right] \end{array} \right.$$

II. Now everywhere $c_K = c_{Cl}$ (only in the boundary-layer an excess of positive or negative Ions is present, owing to the formation of the doublelayer), therefore also

$$\frac{c_{K_2}}{c_{K_1}} = \frac{c_{Cl_2}}{c_{Cl_1}},$$

and so we find ¹⁾ by addition of the two equations (5):

$$\Delta = \frac{1}{2\varepsilon} \left[(\mu'_{Cl_2} - \mu'_{Cl_1}) - (\mu'_{K_2} - \mu'_{K_1}) \right] \dots \dots \dots (6)$$

From this last relation it follows at once, that in *dilute* solutions, where the quantities μ' are almost independent of the concentration, the potential-difference Δ will be also independent of the concentration. Whether much or little KCl is distributed through the two solvents, we will always notice about the *same* potential-difference Δ .

If we deduct the two equations from each other instead of adding, then we obtain (observing that $\frac{c_{K_2}}{c_{K_1}} = \frac{c_{Cl_2}}{c_{Cl_1}}$):

$$RT \log \frac{c_{K_2}}{c_{K_1}} = -\frac{1}{2} \left[(\mu'_{Cl_2} - \mu'_{Cl_1}) + (\mu'_{K_2} - \mu'_{K_1}) \right] \dots \dots (7)$$

If now we put

$$\left. \begin{array}{l} \mu'_{K_2} - \mu'_{K_1} = RT \log K_K \\ \mu'_{Cl_2} - \mu'_{Cl_1} = RT \log K_{Cl} \end{array} \right\} \dots \dots \dots (a)$$

in which K_K and K_{Cl} are quantities, which depend on the nature of the two solvents (and which in *dilute* solutions will only be functions of *temperature*) — they are the so-called *partition-coefficients* of the positive and negative Ions — then (6) and (7) pass into

$$\Delta = \frac{RT}{2\varepsilon} \log \frac{K_{Cl}}{K_K} \dots \dots \dots (6a)$$

$$\underline{\left(\frac{c_{K_1}}{c_{K_2}} \right)^2} = K_K \times K_{Cl} \dots \dots \dots (7a)$$

¹⁾ The formula (6) was given already, though with a somewhat different notation, by LUTHER [Z. f. Ph. Ch. **19**, 537 (1896)]. The first thermodynamic theory of the equilibrium of partition was given by me in a paper of 1895 (Z. f. Ph. Ch. **18**, 264—267).

NERNST's formula for Δ , obtained in a different manner, is identical with our formula (5). (As NERNST's $E = V_1 - V_2$, our $\Delta = -E$). For if we replace $\mu'_{K_2} - \mu'_{K_1}$ by $RT \log K_K$ and $\mu'_{Cl_2} - \mu'_{Cl_1}$ by $RT \log K_{Cl}$, then (5) passes into

$$\Delta = - \frac{RT}{\epsilon} \log K_K \frac{c_{K_2}}{c_{K_1}} = \frac{RT}{\epsilon} \log K_{Cl} \frac{c_{Cl_2}}{c_{Cl_1}},$$

and this is NERNST's expression. As has already been observed, the quantities K_K and K_{Cl} are the so-called "partition-coefficients" of the positive and negative Ions. For instance for the positive Ions we should have, when equilibrium of partition occurs:

$$\mu_{K_2} - \mu_{K_1} = 0,$$

or

$$\mu'_{K_2} - \mu'_{K_1} + RT \log \frac{c_{K_2}}{c_{K_1}} = 0,$$

so that we obtain $\frac{c_{K_1}}{c_{K_2}} = K_K$. The same for the negative Ions.

The relation, given by NERNST¹⁾

$$K_K \times K_{Cl} = \frac{C_1}{C_2} \times K_{KCl},$$

in which K_{KCl} is the coefficient of partition of the neutral KCl -molecules, and C_1 and C_2 are the *dissociation* constants in the two phases, follows directly from the thermodynamical meaning of these quantities. For if we write this relation in the form

$$RT [\log K_K + \log K_{Cl}] = RT [\log C_1 - \log C_2 + \log K_{KCl}],$$

it passes, taking into account equation (a) and the relations

$$RT \log K_{KCl} = \mu'_{KCl_2} - \mu'_{KCl_1}; \quad RT \log C_1 = \mu'_{KCl_1} - \mu'_{K_1} - \mu'_{Cl_1};$$

$$RT \log C_2 = \mu'_{KCl_2} - \mu'_{K_2} - \mu'_{Cl_2},$$

immediately into the identity

$$\begin{aligned} (\mu'_{K_2} - \mu'_{K_1}) + (\mu'_{Cl_2} - \mu'_{Cl_1}) &= (\mu'_{KCl_1} - \mu'_{K_1} - \mu'_{Cl_1}) - \\ &- (\mu'_{KCl_2} - \mu'_{K_2} - \mu'_{Cl_2}) + (\mu'_{KCl_2} - \mu'_{KCl_1}). \end{aligned}$$

Not the formula (5), but the formula (6) or (6a), derived by us from (5), deserves however the preference, because the concentrations of the Ions have been eliminated therein, and an expression has been obtained, in which only the coefficients of partition K_K and K_{Cl} occur.

III. If the dissolved electrolyte has now distributed itself so, that

¹⁾ Z. f. Ph. Ch. 8, 138 (1891).

the total concentration is c_1 in A_1 and c_2 in A_2 , we shall have:

$$c_{K_1} = \alpha_1 c_1 \quad ; \quad c_{K_2} = \alpha_2 c_2,$$

in which the quantities c_1 and c_2 may be found by chemical analysis, and α_1 and α_2 by determinations of the conductivity. As soon as Δ can be determined by experiment, $\frac{K_{Cl}}{K_K}$ may be calculated from the equation (6a), and $K_K \times K_{Cl}$ from (7a), and we can therefore get to know separately the quantities K_K and K_{Cl} , consequently also the quantities

$$\mu'_{K_2} - \mu'_{K_1} \quad \text{and} \quad \mu'_{Cl_2} - \mu'_{Cl_1}.$$

From (6a) it further follows, that Δ will be *positive* (as supposed in the figure), when

$$K_{Cl} > K_K.$$

Only when by accident $K_{Cl} = K_K$, Δ can be 0. *In general a potential difference will always occur between two non-miscible solvents, when an electrolyte is partitioned between them.* This potential-difference is given by (6a).

From the equation (7a) it follows, that the relation of the concentrations of the *Ions* in the two solvents in the case of *dilute* solutions will be practically independent of the total concentrations. This equation may also be deduced directly from (3). For this, being a result of (1) and (2), that is to say of the equilibrium of partition and the two equilibria of dissociation, may be written:

$$(\mu'_{K_2} - \mu'_{K_1}) + (\mu'_{Cl_2} - \mu'_{Cl_1}) = -RT \left[\log \frac{c_{K_2}}{c_{K_1}} + \log \frac{c_{Cl_2}}{c_{Cl_1}} \right],$$

and this after substitution passes at once into (7a). For

$$\log \frac{c_{K_2}}{c_{K_1}} + \log \frac{c_{Cl_2}}{c_{Cl_1}} = 2 \log \frac{c_{K_2}}{c_{K_1}} = - \log \left(\frac{c_{K_1}}{c_{K_2}} \right)^2.$$

The equations (6a) and (7a) moreover lead to an important conclusion.

As the quantities K_K and K_{Cl} are, in the case of *dilute* solutions, *specific* quantities, we must therefore find about the *same values* for these quantities in the case of *other* salts, when employing the same solvents A_1 and A_2 . For NaCl for instance we will have:

$$\Delta' = \frac{RT}{2\varepsilon} \log \frac{K_{Cl}}{K_{Na}}; \quad \left(\frac{c_{Na_1}}{c_{Na_2}} \right)^2 = K_{Na} \times K_{Cl},$$

from which by experimental determination of Δ' and the quantities c_{Na_1} and c_{Na_2} , the two quantities K_{Na} and K_{Cl} may be determined. The value, found for K_{Cl} from KCl-solutions in A_1 and A_2 , must then be practically *identical* with the value for K_{Cl} , determined from solutions of NaCl in these solvents.

The quantities Δ will show an almost complete additive character, on account of K_K and K_{Cl} being independent of the concentration in the case of dilute solutions. For instance, in the same solvents A_1 and A_2 we must find:

$$\Delta_{KCl} - \Delta_{NaCl} = \Delta_{KNO_3} - \Delta_{NaNO_3}.$$

And the same for other combinations.

The above considerations may be readily extended to the case of *non-binary* electrolytes such as $CaCl_2$, $ZnCl_2$, etc. In the different equations the valencies ν of the Ions will then also occur, because the fundamental relation (4) then passes into the more general one:

$$\Delta = - \frac{\begin{matrix} + & + \\ \mu_2 - \mu_1 \\ + \\ \nu \epsilon \end{matrix}}{=} = \frac{\begin{matrix} - & - \\ \mu_2 - \mu_1 \\ - \\ \nu \epsilon \end{matrix}}{=}.$$

IV. The question in how far and in what manner the value of Δ , given in (6) or (6a), is still dependent on the concentrations of the Ions, can only be answered, when we calculate the values of μ'_{K_1} etc. with the aid of an equation of condition. If we accept the equation of VAN DER WAALS as also applying to liquid-phases, we obtain for instance for the molecules n_p :

$$\begin{aligned} \mu_p = & -k_p T (\log T - 1) - RT \left(\log \frac{V-b}{n_1} - 1 \right) + [(e_p)_0 - T(\eta_p)_0] + \\ & + RT \frac{\sum n_1}{V-b} b_p - \frac{2}{V} (n_1 a_{p1} + n_2 a_{p2} + \dots) + RT \log \frac{n_p}{n_1}. \end{aligned}$$

n_1 stands here for the molecular number of the solvent. For b and a we write:

$$\begin{aligned} b &= n_1 b_1 + n_2 b_2 + \dots \\ a &= n_1^2 a_{11} + 2 n_1 n_2 a_{12} + 2 n_1 n_3 a_{13} + \dots \end{aligned}$$

Let us now calculate the value of

$$(\mu'_{Cl_3} - \mu'_{Cl_1}) - (\mu'_{K_2} - \mu'_{K_1}),$$

or, what amounts to the same, of

$$(\mu'_{K_1} - \mu'_{Cl_1}) - (\mu'_{K_2} - \mu'_{Cl_2}).$$

If we indicate the solvent by the index 1, the non-dissociated KCl , dissolved therein, by 2, the two Ions by 3 and 4, we obtain for $\mu'_{K_1} - \mu'_{Cl_1}$ the expression

$$\begin{aligned} & - (k_3 - k_4) T (\log T - 1) + [(e_3)_0 - (e_4)_0] - T[(\eta_3)_0 - (\eta_4)_0] + \\ & + RT \frac{\sum n_1}{V-b} (b_3 - b_4) - \frac{2}{V} [n_1 (a_{31} - a_{41}) + n_2 (a_{22} - a_{42}) + n_3 (a_{33} - a_{43}) + n_4 (a_{34} - a_{44})]. \end{aligned}$$

Remembering, that $n_3 = n_4$, $a_{34} = a_{43}$, the last term may be simplified to

$$-\frac{2}{V}[n_1(a_{31}-a_{41}) + n_2(a_{32}-a_{42}) + n_3(a_{33}-a_{44})].$$

For $\mu'_{K_2} - \mu'_{Cl_2}$ we find a similar expression. In this, however, the quantities k_3 , k_4 (the heat-capacities of the same Ions, at infinite volume) and $(e_3)_0$, $(e_4)_0$, $(\eta_3)_0$, $(\eta_4)_0$ (the energy and entropy-constants of these Ions) will be exactly the same. a_{32} , a_{42} , a_{33} and a_{44} will also remain unaltered, so that for the difference $(\mu'_{K_1} - \mu'_{Cl_1}) - (\mu'_{K_2} - \mu'_{Cl_2})$ we may write:

$$RT \left[\frac{\sum n'_1(b_3-b_4)}{V-b} - \frac{\sum n'_1(b'_3-b'_4)}{V'-b'} \right] - 2 \left[\left(\frac{n_1(a_{31}-a_{41})}{V} - \frac{n'_1(a'_{31}-a'_{41})}{V'} \right) + (a_{32}-a_{42}) \left(\frac{n_2}{V} - \frac{n'_2}{V'} \right) + (a_{33}-a_{44}) \left(\frac{n_3}{V} - \frac{n'_3}{V'} \right) \right].$$

The quantities, relating to the second solvent, are indicated by accents.

We may now go a step further and accept as a first approximation:

$$b_3 = b_4, \quad b'_3 = b'_4, \quad a_{33} = a_{44}.$$

If we then also write

$$\frac{V}{n_1} = v, \quad \frac{V'}{n'_1} = v', \quad n_2 = n(1-\alpha), \quad \frac{n}{n_1} = c, \text{ etc.,}$$

we finally obtain for Δ :

$$\Delta = \frac{1}{\varepsilon} \left[\left(\frac{a'_{31}-a'_{41}}{v'} - \frac{a_{31}-a_{41}}{v} \right) + (a_{32}-a_{42}) \left(\frac{(1-\alpha)c'}{v'} - \frac{(1-\alpha)c}{v} \right) \right]. \quad (6b)$$

As, in consequence of the equilibrium of partition, $\frac{(1-\alpha)c'}{(1-\alpha)c}$ is constant, Δ will have the form

$$\Delta = \Delta_0 + \lambda(1-\alpha)c,$$

or since, on account of the equilibrium of dissociation, $\frac{(ac)^2}{(1-\alpha)c} =$ constant, also the form

$$\Delta = \Delta_0 + \lambda'(\alpha c)^2.$$

Whether Δ will be positive or negative, depends chiefly on Δ_0 . If

$$\frac{a_{31}-a_{41}}{v} < \frac{a'_{31}-a'_{41}}{v'},$$

Δ will be positive. We also see, that $\Delta - \Delta_0$ will increase or decrease with the *second* power of αc , that is to say in the case of strongly dissociated electrolytes, where α is nearly 1, almost with c^2 .

Dec. 1902.

Physics. — Dr. J. J. HALLO: “*The value of some magneto-optic constants.*” (Communicated by Prof. P. ZEEMAN).

In my doctoral thesis, on *The magnetic rotation of the plane of polarisation in the neighbourhood of an absorption-band*¹⁾, I have calculated the values which three of the constants, occurring in VOIGT's theory of magneto-optic phenomena, assume in a particular case. I did not then know as yet, that DRUDE had already tried — in his *Lehrbuch der Optik* (Leipzig, 1900) — to make some estimate as to the order of magnitude of a constant r , introduced by him, which is connected in a simple manner with one of the constants of VOIGT's theory, of which I have determined the value. Therefore I beg to be allowed to mention here my results and those of DRUDE, and to examine in how far these results agree.

If \mathfrak{X} , \mathfrak{Y} , \mathfrak{Z} are the components of the electric polarisation in some medium, VOIGT assumes that every one of these components exists of a part X , Y , Z , relating to the free ether, and a series of other parts \mathfrak{X}_h , \mathfrak{Y}_h , \mathfrak{Z}_h , indicating the state of the ponderable matter. He therefore assumes:

$$\mathfrak{X} = X + \sum \mathfrak{X}_h, \text{ etc.}$$

A representation of the phenomena of selective absorption, in which the influence of a magnetic field with components A , B , C is also taken into account, is gained when the sets of vector-components A , B , C are subjected to the conditions:

$$\mathfrak{X}_h + a_h \frac{\partial \mathfrak{X}_h}{\partial t} + b_h \frac{\partial^2 \mathfrak{X}_h}{\partial t^2} + c_h \left(C \frac{\partial \mathfrak{Y}_h}{\partial t} - B \frac{\partial \mathfrak{Z}_h}{\partial t} \right) = \epsilon_h X, \text{ etc.}$$

The constant b_h appears to be equal to $\tau_h^2/4\pi^2$, if τ_h is the vibratory period of a free vibration of the absorbing medium; I have derived the values of the constants a_h , c_h and ϵ_h for the line D_2 from the results of my measurements in a particular case (for a flame which contained very much sodium); the values I have found are (*vide* p. 85 of my thesis):

$$a_h = 1 \cdot 10^{-20};$$

$$c_h = 0,2 \cdot 10^{-23};$$

$$\epsilon_h = 7,5 \cdot 10^{-8}.$$

The constants a_h and ϵ_h depend on the density of the sodium-vapour in the flame, the constant c_h does not so far as we know.

The data which served for the calculation of these constants are the following: a_h was calculated from the width of the absorption-

¹⁾ Amsterdam, 1902.

band, which is proportional to it; this width was about 1 Angström Unit; c_h was calculated from the magnitude of the ZEEEMAN-effect; for this magnitude in the field which I used — of 9000 C. G. S. Units — I took $\frac{1}{20}$ part of the interval between the two sodium-lines; ϵ_h was calculated from the value of the rotation of the plane of polarisation in the neighbourhood of the absorption-band; on the magnitude of this rotation as a function of the wavelength, for different intensities of the magnetic field and different widths of the absorption-bands, I have made measurements of which the results have been recorded in the tables given in my thesis. From these tables I shall quote one series here, giving the numbers from which the above-mentioned value of ϵ_h was deduced (*vide* p. 42 of my thesis, table 24 I):

σ	χ	σ	χ
15	88	50	41
20	51	55	40
25	31	60	9
30	23	65	8
35	18	70	6
40	14	75	5
45	12		

Here σ is proportional to the difference between the wavelength of a given kind of light and the wavelength which corresponds with the middle of the line D_2 ; the coefficient of proportion may be found from the fact that the difference between the wavelengths of the two sodiumlines corresponds with a value $\sigma=130$; χ represents the rotation of that particular kind of light in my experiments, expressed in a unit of which the value is determined by the fact that a rotation of 180° corresponds with a value $\chi=105$. Thus we read from the series, given above, that for a value of σ corresponding with $\frac{35}{130} \times 6$ A. U. the rotation of the plane of polarisation is $\frac{18}{105} \times 180^\circ$; from these corresponding numbers the value of ϵ_h is deduced in the way which I explained in my thesis.

DRUDE, in his *Lehrbuch der Optik* which I mentioned above (p. 353), in his version of the theory of dispersion gives the equations of motion of an electron in the form:

$$m \frac{\partial^2 \xi}{\partial t^2} = eX - \frac{4\pi e^2}{\mathfrak{D}} \xi - r e^2 \frac{d\xi}{dt}.$$

Here m is the mass, e the charge of the electron, ξ its displacement parallel to the axis of X from a position of equilibrium, X the component parallel to this axis of the external electric force acting on the electron; r and \mathfrak{D} are positive constants.

In working out the theory it appears that VOIGT's constant a_h is identical with the expression $r\mathfrak{D}/4\pi$ of DRUDE. Now the value of \mathfrak{D} was calculated by DRUDE himself (p. 490) from the vibratory period of the sodiumlines; he finds the value of this constant to be $7,6 \cdot 10^{-23}$; from this value and that of VOIGT's constant a_h which I mentioned just now, we find:

$$r = 1650;$$

here we must bear in mind that this value applies to the particular sodiumflame to which my measurements relate; r must, as well as a_h , depend on the density of the sodiumvapour in the flame.

DRUDE tries in his book to fix limits, between which the value of r must lie. He finds a lower limit by deducing from theory the proportion between the quantity of light, which the absorbing sodiumflame itself begins to emit under the influence of incident radiation, and the quantity of incident light which is absorbed. This proportion he finds to be $0,126/r$. From the fact that reversal of a sodiumline is possible, he concludes that this proportion must be considerably smaller than 1, and he therefore fixes the lower limit for the value of r by assuming:

$$r > 10.$$

A higher limit is found by DRUDE from the consideration of the phenomena of interference. He deduces theoretically the value of the coefficient of damping γ of the free vibrations of the electron and finds for this:

$$\gamma = 0,6 \cdot r \cdot 10^{-7}.$$

Now this coefficient must be small, as with great phase-differences interference-phenomena can still be observed. With sodiumlight interference-phenomena have been observed with a phase-difference corresponding with 200000 wavelengths; therefore 200000 γ must still be smaller than 1, therefore in this case:

$$r < 100.$$

It is evident that this result is not at all incompatible with the value of r which I calculated above. In order to observe interference-phenomena with such great phase-differences it has been necessary to use a source of light showing very narrow sodiumlines; with

the width of the sodiumlines to which my measurements relate (which was about 1 Angström-Unit) the greatest phase-difference with which interference-phenomena can be observed is one corresponding with 3000 wavelengths; the higher limit is therefore raised to 7000, so that r must in this case lie between 10 and 7000, which it really does according to the calculations given above.

Some further deductions which can be made from the comparison of VOIGT's equations with those given by DRUDE, have already been given on pp. 90—95 of my doctoral thesis, with reference to LORENTZ's paper in the Report of the *Congrès International de Physique*, held in Paris in 1900, and I will here only refer the reader to that part of my thesis.

Physiology. — “*A new law concerning the relation between stimulus and effect.*” V. By Dr. J. K. A. WERTHEIM SALOMONSON.
(Communicated by Prof. C. WINKLER.)

From the law connecting excitation and effect,

$$E = A(1 - \epsilon^{-B(R-C)}) \quad . \quad . \quad . \quad . \quad . \quad (1)$$

we may obtain by differentiating

$$\frac{dE}{dR} = AB\epsilon^{-B(R-C)}$$

or also

$$dR = \frac{dE}{AB} \epsilon^{B(R-C)} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Introducing differences instead of differentials, with this limitation that the differences should be very small, and taking according to FECHNER, ΔE , the differential sensation-threshold as a constant quantity, we obtain

$$\Delta R = k_1 \epsilon^{B(R-C)} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

or, by putting the constant $\epsilon^{-BC} k_1 = k$

$$\Delta R = k \epsilon^{BR} \quad . \quad . \quad . \quad . \quad . \quad (4)$$

the latter formula containing an expression for the absolute differential threshold-value. We might employ this formula for psychical impressions of peripheral stimuli, if the peripheral stimulus had caused excitation of only peripheral neurones with equal stimulation-constants B , and moreover if all these neurones had been uniformly stimulated. Under a similar limitation we might also admit the validity of the formula for the relative differential threshold-value deduced from (4) by dividing both terms by R ; we then obtain:

$$\frac{\Delta R}{R} = k \frac{\epsilon^{BR}}{R} \dots \dots \dots (5)$$

As a rule, however, this formula may not be applied in the case of psychical processes, because the above-stated conditions have not been fulfilled. It is impossible to suppose the case of a peripheral stimulus hitting only one single peripheral neuron, or of one single group of neurones being exposed uniformly and with equal force to that stimulus.

Let us see, what happens when a sense-organ in the living human organism is subjected to a stimulus. For instance we may consider the action of pressure on the skin.

Suppose the compressing object to be in contact with a limited surface of the skin at the moment the pressure commences. We

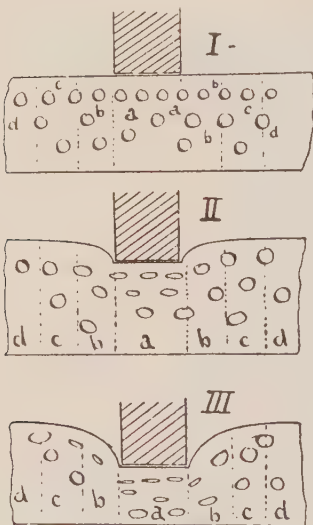


Fig. 1.

may take it for granted that all end-organs situated within the limited skin-surface in direct contact with the compressing object, undergo an equal and uniform pressure, and that in the case of this pressure being increased, its action will remain uniform. To the neurones connected with the nerve terminations *a, a, a, a*, our deduced law (5) may be therefore applied. As soon as the pressure increases the skin-surface will undergo a change of shape and be compressed (see fig. 1). This implies that nerve-endings *b, b*, situated outside of the originally compressed surface, will also enter into an excitatory state. If this deformation be a slight one, only the nearest end-organs *b, b* will be

compressed. By increased pressure the more distantly situated ones *c, c, d, d* etc. will also be stimulated. To all these end-organs, situated outside of the originally compressed surface, impulses are given, which are conducted to the central nervous system. From all the combined impressions finally results the sensation by which our judgment is decided.

The neurones connected with *b, b, c, c, d, d* etc. will likewise obey the law of stimulation and effect. The intensity of stimulus however is different for all these neurones, and also different from that for the neurones *a, a, a*. Therefore, whilst for the neurones *aaa*, the expression

$$\varrho = \frac{dR}{R} = k \frac{\epsilon^{BR}}{R}$$

might be employed, we must use for the neura b, b, c, c, d, d etc. the expression

$$\varrho_1 = K \frac{\epsilon^{Br_1}}{r_1}, \quad \varrho_2 = K \frac{\epsilon^{Br_2}}{r_2}, \quad \varrho_3 = K \frac{\epsilon^{Br_3}}{r_3} \text{ etc.}$$

As the stimuli r_1, r_2, r_3 etc. are proportional to R , we may substitute for these $m_1 R, m_2 R, m_3 R$ etc.

The question arises next: how shall we psychically combine these impressions in order to make use of them for the special purpose aimed at by our experiment, i. e. to decide whether two stimuli are different from one another? Summation or addition is out of the question: this would be in contradiction with the experience that by fixing our attention on a definite sensation, other sensations are weakened. It is clear that we will conform our judgment to that part of the sensation that is best fit for our purpose. Starting from this fact we may continue to treat the question mathematically.

In the first place it ought to be taken into consideration, that by increment of a stimulus not a small number of new peripheral neurones are stimulated, but generally a great many. In the case of a pressure e.g. not only nerve-endings lying sideways of the compressed surface, but also more profoundly situated end-organs will be acted upon by increased intensity of stimulus. For every individual neuron we shall have to put in another coefficient m . If

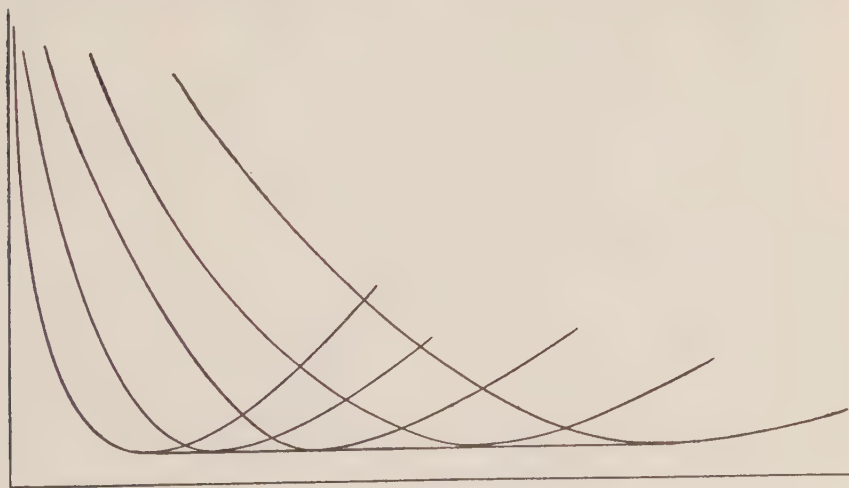


Fig. 2.

we construct therefore a great many curves $\varrho_1, \varrho_2, \varrho_3$ all these curves will only be different on account of the constant m being changed. We now suppose the final judgment fixed each time by a part of a farther situated curve. Thence it may be concluded, that the

enveloping curve will represent the manner in which a judgment about the final result originates. To obtain the envelope of the group of curves $\varphi = K \frac{\epsilon^{mBR}}{mR}$, if the constant m is changed, we put:

$$F = \varphi - K \frac{\epsilon^{mBR}}{mR} \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

Calculating the value of m corresponding to $\frac{\partial F}{\partial m} = 0$, and substituting this value into the equation $F = 0$, we find the formula for the enveloping curve. We may state:

$$\frac{\partial F}{\partial m} = -\frac{K}{R} \cdot \epsilon^{mBR} \cdot \frac{mBR-1}{m^2} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

From which follows $m = \frac{1}{BR}$, which substituted into $F = 0$, gives:

$$\varphi = KB\epsilon \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

proving that the *relative differential thresholdvalue is constant*.

By this process we have deduced from our formula the law of WEBER.

From our deduction may be inferred that the area, wherein the law of WEBER prevails, is a limited one. The validity of this law commences within the area of the enveloping curve, and a look on the figure 2, will make it clear that the first part of the whole sensation-curve is given by the descending part of the curve

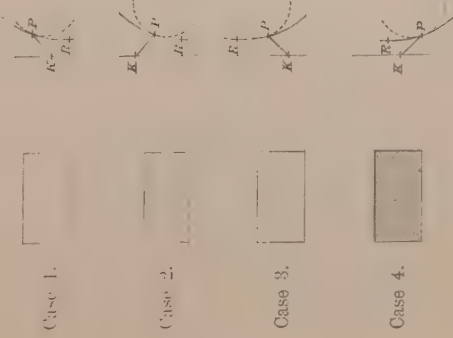
$\varphi = K \frac{\epsilon^{BR}}{R}$. The horizontal part then represents the area within the limits of which the law of WEBER prevails, whilst in the case of very great intensities of stimuli the ascending part of the curve $\varphi = K \frac{\epsilon^{BmR}}{mR}$ will appear.

There remains still another conclusion to be drawn from our deduction. This latter was founded on the supposition that the increment-constant B was the same for all stimulated neurones. This, however, is highly improbable; in the most favourable cases we may only suppose that the B -coefficient of the homogenous neurones will possess approximatively the same value, from which follows that we may admit the law of WEBER at best as an approximation.

Finally it may be mentioned here that apart from the above-demonstrated correction for obtaining an approximation in the direction of the law of WEBER-FECHNER, probably still another means of correction exists in some of our sense-organs; I shall prove this in a later communication.

SIDE OF THE LARGE VOLUMES.

Temperature slightly *higher* than the critical temperature of the solvent.



Case 1.

Case 2.

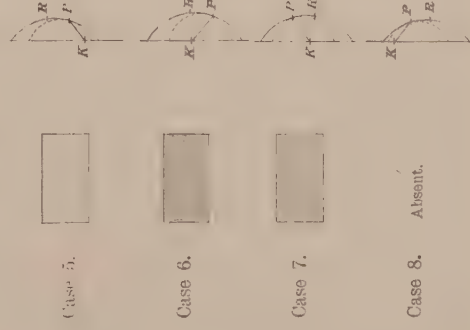
Case 3.

Case 4.

SIDE OF THE LARGE VOLUMES.

Temperature slightly *lower* than the critical temperature of the solvent.

Fig. 1.



Case 5.

Case 6.

Case 7.

Case 8.

Absent.

The figures relate to the ψ , x diagram.

K is the critical point of the solvent.

P the plaitpoint.

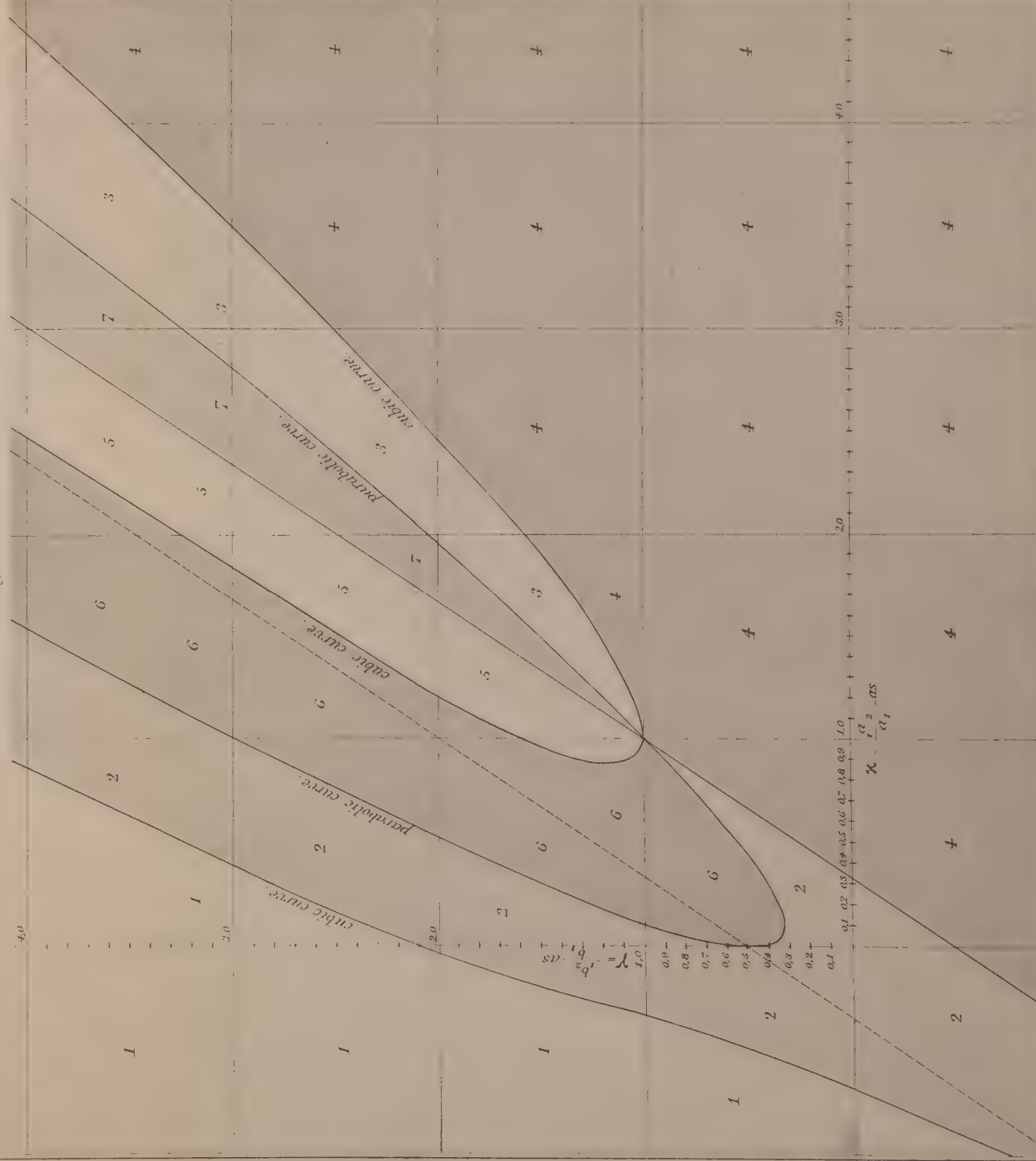
R the critical point of contact

KP indicates the direction of the plait-point curve.

The traced curve represents the connodal curve.

The dotted curve represents the spinodal curve.

Fig. 2.



Physics. — “*Plaitpoints and corresponding plaits in the neighbourhood of the sides of the ψ -surface of VAN DER WAALS.*” By Prof. D. J. KORTEWEG.

(Communicated in the Meeting of December 27, 1902).

FIRST DESCRIPTIVE PART.

1. As in my “*Théorie générale des plis*”¹⁾ I wish to precede in this paper the demonstrating part by a short summary of the obtained results.

As we know a plaitpoint may occur on the side $x=0$ of the ψ -surface of VAN DER WAALS,²⁾ which is represented by the equation:

$$\psi = -MRT \log(v - b_x) - \frac{a_x}{v} + MRT \{x \log x + (1-x) \log(1-x)\} \quad (1)$$

where:

$$a_x = a_1(1-x)^2 + 2 {}_1a_2 x(1-x) + a_2 x^2 = a_1 + 2({}_1a_2 - a_1)x + (a_1 + a_2 - 2 {}_1a_2)x^2, \dots \quad (2)$$

$$b_x = b_1(1-x)^2 + 2 {}_1b_2 x(1-x) + b_2 x^2 = b_1 + 2({}_1b_2 - b_1)x + (b_1 + b_2 - 2 {}_1b_2)x^2, \dots \quad (3)$$

This occurs only in the case that the temperature T corresponds with the critical T_k of the principal component; but in that case it occurs always. This plaitpoint coincides with the critical point of the principal component for which $v = 3 b_1$ and which in our figures we shall always represent by the symbol K ; the plaitpoint itself will be represented by P .

If the temperature varies, the plaitpoint and the corresponding plait can in general behave in two quite different ways. It will namely either, as is indicated by the *first* four cases on fig. I of the plate, on which the (v, x) projections of the sides of the ψ -surface are represented, at increase of temperature leave the v -axis and move to the inner side, therefore entering the surface, and disappear from the surface at decrease of temperature, or it will as in the *last* four cases of that figure, enter the surface at decrease and leave it at increase of temperature.

¹⁾ Archives Néerlandaises, T. 24 (1891) p. 295—368: La théorie générale des plis et la surface ψ de VAN DER WAALS dans le cas de symétrie. See there p. 320—368.

²⁾ We take here the equation of the ψ -surface as it has been originally derived by VAN DER WAALS, so without the empiric corrections which seem to be required to make the results agree quantitatively better with the experimental data. So is, for instance, a_x considered to be independent of the temperature, and all the results and formulae mentioned are founded on this supposition. It would not have been difficult to take such empiric corrections into account, as has really been done by VERSCHAFFELT and KEESOM in their papers, to which we shall presently refer; but then the results were of course not so easily surveyed. Therefore I have preferred to leave them out of account, at least for the present.

And this different behaviour of the plaitpoint will necessarily be accompanied by a different behaviour of the connodal and spinodal curves. For they must always cut the v -axis at decrease of temperature, the connodal in the points of contact of the double tangent of the ψ, v -curve of the principal component, the spinodal in its two points of inflection; at increase of temperature above the critical temperature of the principal component, however, they get quite detached from the v -axis. In connection with this they turn in the first four cases of fig. 1 their convex sides, in the last four cases their concave sides towards the side $x = 0$ of the ψ -surface as is also indicated in the figure, where the connodal curves are traced, the spinodal curves dotted.

Fig. a.



At *decrease* of temperature a figure originates in the *first* four cases as is schematically given here in Fig. a. At *increase* of temperature, on the contrary, in the *last* four cases, the spinodal and connodal curves disappear from the surface at the same time with the plaitpoint itself.

Besides to this different behaviour it appeared however desirable, to pay attention to two other circumstances. *First* to the direction of the tangent in the plaitpoint, whether if prolonged towards the side of the large volumes, it inclines to the *inner* side of the ψ -surface, as in cases 1, 2, 5 and 6 of fig. 1, or whether it inclines to the *outer* side, as in the remaining four cases. For on this it will depend which of the two kinds of retrograde condensation will eventually appear ¹⁾. But besides we have to pay attention to the question whether the plaitpoint, entering the ψ -surface, either at decrease or increase of temperature, will move towards the side of the larger volumes as in cases 1, 3, 5 and 7, or whether it will move towards that of the smaller volumes as in the other cases. In connection with this question we may point out here that the line KP in fig 1 of the plate may everywhere be considered as a small chord of the plaitpoint curve of the v, v -diagram and accordingly indicates the initial direction of that curve, which it has when starting from point K .

The three different alternatives, which we have distinguished in this way, give rise to the eight cases represented in fig. 1, and we may now raise the question on what it will depend which of these eight cases will occur at a given principal component with a given

¹⁾ See on these two kinds of retrograde condensation inter alia, the paper of VAN DER WAALS: "Statique des fluides (Mélanges)": in Tome I of the "Rapports présentés au congrès international de physique, réuni à Paris en 1900", page 606—609.

admixture; of course only in so far as with sufficient approximation the conditions are satisfied on which the derivation of the equation (1) of VAN DER WAALS rests.

2. The answer to this question is given in the graphical representation of fig. 2. It appears, namely, that the case which will occur, is exclusively determined by the quantities $\frac{1a_2}{a_1} = \alpha$ and $\frac{1b_2}{b_1} = \gamma$, which have already played a prominent part in my above mentioned "*Théorie générale des plis*."

In accordance with this a α - and a γ -axis are assumed in fig. 2 of the plate and the regions where the points are situated whose α - and γ -values give rise to the appearance of each of these cases, are distinguished by different numbers and colours.

For instance the white region 1 indicates the α - and γ -values for which the plaitpoint enters the ψ -surface at rising temperature, moving from K to the side of the large volumes, while in the well-known way we can derive from its situation on the connodal curve on the right above the critical point of contact R (for which the tangent to the connodal curve runs parallel with the v -axis) that the retrograde condensation will be eventually of the second kind (i. e. with temporary formation of vapour) and also that the temporary vapour phase will have a larger amount of admixture than the permanent denser phase.

In the same way the blue field 5 indicates the α - and the γ -values for which the plaitpoint enters the ψ -surface at decrease of temperature, moving towards the side of the large volumes; whilst the retrograde condensation will be of the first kind and the temporary denser phase will show a smaller proportion of admixture than the permanent vapour phase.

3. When examining this graphical representation we see at once that one of the eight regions which were à priori to be expected, region 8, fails. From this follows that for normal substances the combination of retrograde condensation of the second kind and of a plaitpoint which enters the surface at decreasing temperature and moves towards the side of the small volumes, is not to be expected.

All the other seven regions, however, are represented in the graphical representation.

4. Further the point $\alpha = 1, \gamma = 1$, is remarkable, where no less than six regions meet. This point represents really a very particular

case, namely that in which the molecules of the admixture, both with regard to volume and to attraction, behave towards the molecules of the principal component exactly as if they were identical with these latter molecules.

If at the same time $a_2 = a_1$, $b_2 = b_1$, which is of course not involved in the above suppositions, it is easy to see that at decrease of temperature below the critical temperature the plait would suddenly appear all over the whole breadth of the ψ -surface.

Now it is true that every deviation from these equalities $a_2 = a_1$, $b_2 = b_1$ will prevent such a way of appearance, but it is evident that then the behaviour of plaitpoint and corresponding plait will depend on a_2 and b_2 , i.e. the first approximation for which the knowledge of κ and γ is sufficient and which everywhere else suffices to make this behaviour known to us up to a certain distance from the side of the ψ -surface, fails here.

And also already in the *neighbourhood* of the combination of the values $\kappa = 1$, $\gamma = 1$, this first approximation will be restricted, to the immediate neighbourhood of the point K and of the critical temperature T_k of the principal component. When we are not in that immediate neighbourhood the influence of a_2 and b_2 , — of the former of these quantities specially, — will soon be felt. On the contrary for values of κ or γ sufficiently differing from unity the considerations derived from the first approximation will probably be of force within pretty wide limits, at least in a qualitative sense.

5. Before proceeding to a discussion of the border curves between the different regions, we will shortly point out that we cannot attach an equally great importance to all the parts of the graphical representation. So all points lying left of the γ -axis relate to negative values of ${}_1a_2$, i.e. to the case that the molecules of principal component and admixture should repel each other, which is not likely to occur.

In the same way the negative values of γ , so of ${}_1b_2$, of the points below the κ -axis, should be considered as having exclusively mathematical signification. If the relation, ${}_1b_2 = \frac{1}{2}(b_1 + b_2)$, should still be applied also for very unequal values of the b 's, then γ would even remain always larger than $\frac{1}{2}$ and so the part below the line $\gamma = \frac{1}{2}$ would lose its physical signification.

6. With regard to the border curves between the different parts, we have first to deal with the parabolic border curve separating the

regions containing blue (blue, green, purple) from the others. It touches the γ -axis in the point $\varkappa=0$, $\gamma=\frac{1}{2}$. Its equation is:

$$(2\gamma - 3\varkappa + 1)^2 - 8(\gamma - \varkappa) = 0$$

or if we transfer the origin to the point $\gamma=1$, $\varkappa=1$ and therefore introduce the new variables: $\varkappa'=\varkappa-1$; $\gamma'=\gamma-1$, which brings about a simplification also for the other border curves, we get:

$$(2\gamma' - 3\varkappa')^2 - 8(\gamma' - \varkappa') = 0. \quad (4)$$

Then we have everywhere inside that parabola, so in the regions 5, 6, 7:

$$(2\gamma' - 3\varkappa')^2 - 8(\gamma' - \varkappa') < 0$$

and outside it in the regions 1, 2, 3, 4:

$$(2\gamma' - 3\varkappa')^2 - 8(\gamma' - \varkappa') > 0.$$

In consequence of this it depends on the situation inside or outside the parabola, whether on the corresponding Ψ -surface the plaitpoint will enter the surface at *decrease* of temperature or at *increase* of temperature and whether the spinodal curves turn their convex or their concave sides to the side $x=0$.

Fig. b.



For points *on* the parabolic border curve the plaitpoint occurring in the point K at the critical temperature of the principal component, is to be considered as an homogeneous double plaitpoint at that moment. The projection on the v , x -surface appears then as is indicated in fig. b.

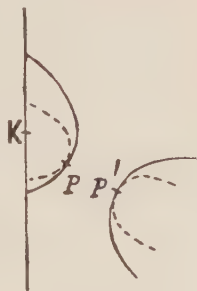
How the transition to this condition takes place may be made clear by the subjoined fig. c, which represents the same projection for a temperature slightly below that of the critical temperature of the principal component

for the case that the \varkappa - and γ -values indicate a point, which is still situated in the green region 6, but on the verge of the border curve of the yellow region 2.

Very near the plaitpoint P we find here already a second plaitpoint P' , which at further decrease of temperature soon coincides with P .

If now the point in the green region approaches the border curve of the yellow region, the two points P coincide nearer and nearer to the critical temperature of the principal component and to the point K . On the border curve it takes place in the point K itself. Beyond the limit, in the yellow region, the plait of P does not develop any more and P' takes the place of P .

Fig. c.



7. As second border we get in the graphical representation the straight line:

$$2\gamma' - 3\kappa' = 0. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

It separates the regions containing red 3, 4 and 7, — for which $2\gamma' - 3\kappa' < 0$, and where the tangent in the plaitpoint, continued in the direction of the large volumes, inclines towards the side $x=0$ — from the others, where it inclines to the inner side of the ψ -surface.

As we saw before, this inclination determines the nature of the retrograde condensation. Not exclusively, however. For in the first four cases of figure 2 the result of the same way of inclination is in this regard exactly the opposite of that in the last four cases; hence the parabolic border curve acts here also as a separating curve; so that retrograde condensation of the first kind (i.e. with temporary formation of the denser phase) occurs in the regions 3, 4, 5 and 6, in the two first with greater proportion of the admixture in the temporary phase, in the two last the reverse, and on the contrary retrograde condensation of the second kind in the regions 1 and 2 (with a larger proportion in the temporary less dense phase) and 7 (with a smaller proportion in that same phase).

8. The third border curve is a cubic curve with the equation:

$$(2\gamma' - 3\kappa')^3 - 4(4\gamma' - 3\kappa')(2\gamma' - 3\kappa') + 16\gamma' = 0. \quad . \quad . \quad (6)$$

It consists of two branches, which possess both on one side the common asymptote:

$$2\gamma' - 3\kappa' - 2 = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

and which run at the other side parabolically to infinity.

The right-side branch, whose shape resembles more or less a parabola, touches the curve $\gamma' = 0$ in the point $\kappa' = 0, \gamma' = 0$ ($x=1, \gamma=1$).

Between the two branches, so in the regions 2, 4 and 6:

$$(2\gamma' - 3\kappa')^3 - 4(4\gamma' - 3\kappa')(2\gamma' - 3\kappa') + 16\gamma' < 0;$$

in all the other regions of course > 0 .

In the former case the tangent KP to the plaitpoint-curve of the (v, x) -diagram is directed to the side of the small volumes, in the second to that of the large volumes.

If we, however, examine, whether e.g. at *decrease* of temperature the plaitpoint moves towards the large or towards the small volumes, the parabolic border curve acts again as separating curve.

It appears then that the plaitpoint moves towards the large volumes at decrease of temperature in the regions 2, 4, 5 and 7, at increase of temperature in the others.

9. The following table gives the characteristics for the different regions.

Region

1	$(2\gamma'-3\kappa')^2-8(\gamma'-\kappa')>0$	$2\gamma'-3\kappa'>0$	$(2\gamma'-3\kappa')^2-4(4\gamma'-3\kappa')(2\gamma'-3\kappa')+16\gamma'>0$
2	>0	>0	<0
3	>0	<0	>0
4	>0	<0	<0
5	<0	>0	>0
6	<0	<0	<0
7	<0	<0	>0

where :

$$\kappa' = \kappa - 1 = \frac{1a_2 - a_1}{a_1}; \gamma' = \gamma - 1 = \frac{1b_2 - b_1}{b_1} \quad \dots \quad (8)$$

A similar tabular survey of the physical properties of the regions seems superfluous, as these properties may be immediately read from the illustrations of fig. 1 of the unfolding plate.

10. It seems not devoid of interest to know how the breadths of the regions change with regard to each other, when continually increasing values of γ' are considered. An inquiry into this shows at once that the blue region 5, measured along a line parallel to the κ -axis, has a limiting value for the breadth of $\frac{2}{3}$. All the other regions mentioned,

however, continue to increase indefinitely, and do this proportional with $\sqrt{\gamma'}$ and in such a way that the yellow and the red region get gradually the same breadth and in the same way the green and the purple one, but that the breadth of the two first mentioned regions will amount to 0,732 of that of the two last mentioned.

If we also take the white region (reckoned e. g. from the γ -axis) into consideration then we find its breadth at first approximation to be proportional with γ' , so that it exceeds in the long run the other mentioned; the orange region keeps of course an infinite breadth.

The limiting values of the ratios may therefore be represented as follows :

$$\frac{\text{white}}{\infty} = \frac{\text{yellow}}{0,732} = \frac{\text{green}}{1} = \frac{\text{blue}}{0} = \frac{\text{purple}}{1} = \frac{\text{red}}{0,732} = \frac{\text{orange}}{\infty} \quad \dots \quad (9)$$

We may see that if we keep κ constant and make γ to increase we always reach the white region, while reversively increase of κ with constant γ leads finally to the orange region. Strong attraction, between the molecules of the admixture and those of the principal

component promotes therefore in the long run the relations of case 4, large volume of the molecules of the admixture promotes those of case 1.

11. We may conclude this descriptive part with mentioning some formulae which we have obtained in the course of our investigation, and which will be derived in the second part. We do not, however, give them as new, as they must essentially agree with similar equations obtained by KEESOM¹⁾ and VERSCHAFFELT²⁾, if the simplifying hypotheses are introduced on which the original equation of the ψ -surface, used by us, rests. Nor does the way in which they are derived, in which the method of the systematic development into series is followed, differ considerably from that of VERSCHAFFELT.

In these formulae we have restricted the number of notations as much as possible. They only hold at approximation in the neighbourhood of point K and of the critical temperature T_k of the principal component.

We shall first give expressions for the radii of curvature $R'_{sp.}$ and $R'_{conn.}$ of the projections on the (v, x) -surface of the spinodal and connodal curves in the plaitpoint; from which appears that the radius of curvature of the connodal curve in the neighbourhood of the point K is at first approximation three times as great as that of the spinodal.

$$R'_{sp.} = \frac{3}{2} b_1^2 [(2\gamma' - 3\kappa')^2 - 8(\gamma' - \kappa')] \dots \dots \dots (10)$$

$$R'_{conn.} = \frac{9}{2} b_1^2 [(2\gamma' - 3\kappa')^2 - 8(\gamma' - \kappa')] = 3R'_{sp.} \dots \dots (11)$$

These radii of curvature are here considered as being positive when both curves turn their convex sides to the v -axis as in the cases 1—4 of fig. 1 and negative in the cases 5—7.

We may shortly point out here that the corresponding radii of curvature on the ψ -surface itself, on account of the strong inclination of the tangential plane in the neighbourhood of the v -axis, are quite different and much smaller, though the relation 1:3, of course

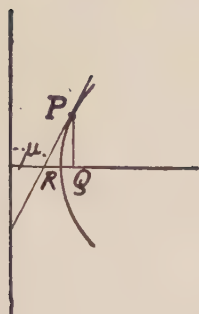
1) W. H. KEESOM. "Contributions to the knowledge of VAN DER WAALS'S ψ -surface. V. The dependence of the plaitpoint constants on the composition in binary mixtures with small proportions of one of the components". Proc. Royal Acad. IV. p. 293—307. Leiden, Comm. phys. Lab. N^o. 75.

2) J. E. VERSCHAFFELT. "Contributions to the knowledge of VAN DER WAALS'S ψ -surface. VII. The equation of state and the ψ -surface in the immediate neighbourhood of the critical state for binary mixtures with a small proportion of one of the components". Proc. Royal Acad. V, p. 321—350, Leiden, Comm. Phys. Lab. N^o. 81.

continues to exist. They even become *zero* when the plaitpoint coincides with the critical point K , so that both curves have then a cusp.

12. The knowledge of the radius of curvature $R_{conn.}$ is of importance specially because it may be used in connection with the formula:

Fig. d.



$$\operatorname{tg} \mu = \mu = \frac{1}{4b_1} (2\gamma' - 3\kappa') x_P, \quad . \quad . \quad . \quad . \quad . \quad (12)$$

through which we know the small angle which the tangent of the plaitpoint forms with the v -axis, to calculate in a very simple way the differences in density and volume between the phases of the plaitpoint P and the critical point of contact R at first approximation¹⁾.

According to fig. *d* we have, within the indicated limit of accuracy:

$$v_P - v_R = PQ = PR = \mu R'_{conn.} = \frac{9b_1}{8} (2\gamma' - 3\kappa') [(2\gamma' - 3\kappa')^2 - 8(\gamma' - \kappa')] x_P \quad . \quad (13)$$

$$x_P - x_R = RQ = \frac{1}{2} \mu^2 R'_{conn.} = \frac{9}{64} (2\gamma' - 3\kappa')^2 [(2\gamma' - 3\kappa')^2 - 8(\gamma' - \kappa')] x_P^2 \quad . \quad (14)$$

13. We proceed now to give the formulae relating to the plaitpoints phase at a temperature T , which does not differ much from the critical temperature T_k of the principal component.

They are:

$$x_P = \frac{4}{(2\gamma' - 3\kappa')^2 - 8(\gamma' - \kappa')} \cdot \frac{T - T_k}{T_k} \quad . \quad . \quad . \quad . \quad . \quad (15)$$

$$v_P - 3b_1 = \frac{3}{8} b_1 \{ (2\gamma' - 3\kappa')^2 - 4(4\gamma' - 3\kappa') (2\gamma' - 3\kappa') + 16\gamma' \} x_P \quad . \quad (16)$$

$$\frac{p_P - p_k}{p_k} = \{ (2\gamma' - 3\kappa')^2 - 4\gamma' + 2\kappa' \} x_P \quad . \quad . \quad . \quad . \quad (17)$$

By means of (15) we may transform (13) and (14), so that they become:

$$v_P - v_R = \frac{9b_1}{2} (2\gamma' - 3\kappa') \frac{T - T_k}{T_k} \quad . \quad . \quad . \quad . \quad (18)$$

and

$$x_P - x_R = \frac{9}{16} (2\gamma' - 3\kappa')^2 x_P \frac{T - T_k}{T_k} \quad . \quad . \quad . \quad . \quad (19)$$

¹⁾ A similar method is given by KEEOM at the conclusion of the before-mentioned paper of VERSCHAFFELT.

to which we add:

$$\frac{p_P - p_R}{p_k} = -\frac{1}{4b_1} (2\gamma' - 3\kappa')^2 (v'_P - v_R) x_P = -\frac{9}{8} (2\gamma' - 3\kappa')^3 \frac{T - T_k}{T_k} x_P \quad (20)$$

14. We shall conclude with giving some formulae relating to coexisting phases, where the index *one* refers to the liquid-, the index *two* to the gas phase. Where the index fails, we may arbitrarily take the value for the one or for the other coexisting phase; either because it is indifferent at the degree of approximation used, or because the formula will equally hold for either state.

$$v_1 = 3b_1 - 3b_1 \sqrt{-4 \frac{T - T_k}{T_k} + [(2\gamma' - 3\kappa')^2 - 8(\gamma' - \kappa')]} x \quad (21)$$

$$v_2 = 3b_1 + 3b_1 \sqrt{-4 \frac{T - T_k}{T_k} + [(2\gamma' - 3\kappa')^2 - 8(\gamma' - \kappa')]} x \quad (22)$$

$$\frac{p - p_k}{p_k} = 4 \frac{T - T_k}{T_k} + 2 (2\gamma' - 3\kappa') x \quad . \quad . \quad . \quad (23)$$

$$x_2 - x_1 = \frac{1}{4b_1} (2\gamma' - 3\kappa') (v_2 - v_1) x \quad . \quad . \quad . \quad (24)$$

$$\begin{aligned} \frac{1}{2} (v_2 + v_1) - 3b_1 = & -\frac{54}{5} b_1 \frac{T - T_k}{T_k} + 3b_1 \left\{ \frac{7}{5} [2\gamma' - 3\kappa')^2 - 8(\gamma' - \kappa')] + \right. \\ & \left. + \frac{1}{8} [(2\gamma' - 3\kappa')^3 - 24(\gamma' - \kappa')(2\gamma' - 3\kappa') + 16(3\gamma' - 2\kappa')] \right\} x \quad . \quad . \quad (25) \end{aligned}$$

in which formula (23) holds also for non-coexisting phases.

SECOND DEMONSTRATING PART.

Transformation of the ψ -surface and preliminary development into series.

15. We begin with a transformation of the ψ -surface by introducing the following variables:

$$v' = \frac{v - 3b_1}{3b_1}; \quad t' = \frac{T - T_k}{T_k}; \quad \psi' = \frac{\psi}{MRT_k}; \quad . \quad . \quad . \quad (26)$$

which means that we henceforth measure the volume v' from the critical volume and with that volume as unit, the temperature in the same way with regard to the critical temperature $T_k = \frac{8a_1}{27b_1MR}$ and the free energy ψ' with MRT_k as unit.

If we moreover put:

$$\frac{a_2 - a_1}{a_1} = \kappa'; \quad \frac{b_2 - b_1}{b_1} = \gamma'; \quad \frac{a_2 - a_1}{a_1} = \lambda'; \quad \frac{b_2 - b_1}{b_1} = \sigma'; \quad . \quad (27)$$

we find easily from (1), (2) and (3) for the equation of the new surface: ¹⁾:

$$\psi' = -(1+t') \log 3b_1 (b_x' + v') - \frac{a_x'}{1+v'} + (1+t') \{x \log x + (1-x) \log (1-x)\}, \quad (28)$$

where

$$a_x' = \frac{9}{8} + \frac{9}{4} \kappa' x - \frac{9}{8} (2\kappa' - \lambda') x^2. \quad . \quad . \quad . \quad (29)$$

$$b_x' = \frac{2}{3} - \frac{2}{3} \gamma' x + \frac{1}{3} (2\gamma' - \sigma') x^2, \quad . \quad . \quad . \quad (30)$$

further:

$$p = -\frac{\partial \psi}{\partial v} = -\frac{MRT_k}{3b_1} \cdot \frac{\partial \psi'}{\partial v'} = -\frac{8}{3} p_k \frac{\partial \psi'}{\partial v'}. \quad . \quad . \quad . \quad (31)$$

16. For investigations in the neighbourhood of the sides it is desirable to develop the expression for ψ' so far as possible according to the powers of x . We write therefore:

$$\psi' = (1+t') x \log x + \chi_0 + \chi_1 x + \chi_2 x^2 + \dots \quad . \quad . \quad (32)$$

where in finite form ²⁾

$$\chi_0 = -(1+t') \log b_1 (2+3v') - \frac{9}{8(1+v')} \quad . \quad . \quad . \quad . \quad (33)$$

$$\chi_1 = (1+t') \left(\frac{2\gamma'}{2+3v'} - 1 \right) - \frac{9\kappa'}{4(1+v')} \quad . \quad . \quad . \quad . \quad (34)$$

$$\chi_2 = (1+t') \left[\frac{2\gamma'^2}{(2+3v')^2} - \frac{2\gamma' - \sigma'}{2+3v'} + \frac{1}{2} \right] + \frac{9(2\kappa' - \lambda')}{8(1+v')} \quad . \quad . \quad . \quad (35)$$

¹⁾ If we wanted to consider a_x as function of the temperature, the simplest way of doing this would be by writing the second term of the second member: $\frac{a'_x(1 + \varepsilon_1 t' + \varepsilon_2 t'^2 + \dots)}{1 + v'}$. The formula $T_k = \frac{8a_1}{27b_1 MR}$ would continue to

hold unmodified for the critical temperature of the principal component, provided we take for a_1 the value it has at that critical temperature. With CLAUSIUS' hypothesis that a_x is inversely proportionate to T , we should get $\varepsilon_1 = -1$; $\varepsilon_2 = +1$. Also (29) continues to hold and the modifications in the developments into series and in the formulae derived from them would be easy to apply.

²⁾ In this form they may be used for investigations concerning the conditions at the side of the ψ -surface at temperatures greatly differing from the critical temperature of the principal component, as are made by KEESOM: Contributions to the knowledge of the ψ -surface of VAN DER WAALS. VI. The increase of pressure at condensation of a substance with small admixtures. Proc. Royal Acad. IV, p. 659—668; Leiden, Comm. phys. Lab. N^o. 79.

or, after development into series with respect to the powers of v' :

$$\chi_0 = -(1+t') \log 2b_1 - \frac{9}{8} - \left(\frac{3}{8} + \frac{3}{2} t' \right) v' + \frac{9}{8} t' v'^2 - \frac{9}{8} t' v'^3 + \\ + \frac{9}{64} (1+9t') v'^4 - \frac{63}{160} v'^6 + \dots \quad (36)$$

$$\chi_1 = (1+t') (\gamma' - 1) - \frac{9}{4} \kappa' - \frac{3}{4} \left[(2\gamma' - 3\kappa') + 2\gamma' t' \right] v' + \\ + \frac{9}{4} \left[(\gamma' - \kappa') + \gamma' t' \right] v'^2 - \frac{9}{8} (3\gamma' - 2\kappa') v'^3 + \dots \quad (37)$$

$$\chi_2 = \frac{1}{2} (1+t') [(1-\gamma')^2 + \sigma'] + \frac{9}{8} (2\kappa' - \lambda') - \frac{3}{8} (4\gamma'^2 - 4\gamma' + 2\sigma' + 6\kappa' - 3\lambda') v' + \dots \quad (38)$$

for which last expression we write:

$$\chi_2 = \sigma_0 + \sigma_1 t' + \sigma_2 v' + \dots \quad (39)$$

Determination of the plaitpoint and classification of the different possible cases.

17. For calculating the coordinates v'_P and x_P of the plaitpoint we have the following relations:¹⁾

$$m \frac{\partial^2 \Psi'}{\partial x^2} + \frac{\partial^2 \Psi'}{\partial v' \partial x} = 0 \quad (40)$$

$$m \frac{\partial^2 \Psi'}{\partial v' \partial x'} + \frac{\partial^2 \Psi'}{\partial v'^2} = 0 \quad (41)$$

$$m^3 \frac{\partial^3 \Psi'}{\partial x^3} + 3m^2 \frac{\partial^3 \Psi'}{\partial v' \partial x^2} + 3m \frac{\partial^3 \Psi'}{\partial v'^2 \partial x} + \frac{\partial^3 \Psi'}{\partial v'^3} = 0 \quad (42)$$

where m represents²⁾ the tangent of the angle formed by the (v', x) -projection of the common tangent of spinodal and connodal curve in the plaitpoint with the v' -axis.

If by means of (32), (36) and (37) we introduce in these equations everywhere the values of the differential quotients at first approximation, in which, as appears, m , x_P and v'_P may be treated as small quantities of the same order, we find:

$$\frac{m}{x_P} - \frac{3}{4} (2\gamma' - 3\kappa') = 0 \quad (43)$$

¹⁾ D. J. KORTEWEG. Ueber Faltenpunkte. Wiener Sitzungsberichte, Bd. 98, Abt. II, (1889), p. 1171.

²⁾ See l. c. p. 1163.

$$-\frac{3}{4}(2\gamma'-3\kappa')m + \frac{9}{4}t' + \frac{9}{2}(\gamma'-\kappa')x_P = 0 \quad . \quad . \quad (44)$$

$$-\frac{m^2}{x_P^2} + \frac{27}{2}(\gamma'-\kappa')m - \frac{27}{4}t' + \frac{27}{8}v'_P - \frac{27}{4}(3\gamma'-2\kappa')x_P = 0, \quad (45)$$

from which it is easy to deduce :

$$m = \frac{3}{4}(2\gamma'-3\kappa')x_P, \quad . \quad . \quad . \quad (46)$$

$$x_P = \frac{4}{(2\gamma'-3\kappa')^2 - 8(\gamma'-\kappa')}t', \quad . \quad . \quad . \quad (47)$$

$$v'_P = \frac{1}{8}[(2\gamma'-3\kappa')^2 - 4(4\gamma'-3\kappa')(2\gamma'-3\kappa') + 16\gamma']x_P, \quad . \quad (48)$$

The formulae (12), (15) and (16) of the first descriptive part of this paper may be derived from these formulae by means of the reverse transformation into the original ψ -surface with the aid of the formulae (26). Applying equation (31) we may also derive formula (17). In the course of this we get first at formula (23), which is given at the end of the descriptive part as serving also for the calculation for coexisting phases. The last statement might be objected to, because for those phases not v' but v'^2 is a quantity of the same order as x and t' ; but this objection loses its force when we observe that in $\frac{\partial \psi'}{\partial v'}$ no term occurs with v'^2 alone.

18. From these formulae (46), (47) and (48) follows now immediately the classification of the plaitpoints according to the eight cases and all the particularities of the corresponding graphical representation, as described in § 2—9. It is only necessary to say a few words about the construction of the cubic border curve.

$$(2\gamma'-3\kappa')^3 - 4(4\gamma'-3\kappa')(2\gamma'-3\kappa') + 16\gamma' = 0. \quad . \quad . \quad (49)$$

A closer examination of this equation shows, namely, that the curve possesses a double point, i.e. the point at infinity of the straight line $2\gamma'-3\kappa'=0$. A simple parameter representation is therefore possible and it is really obtained by putting

$$2\gamma'-3\kappa' = s \quad . \quad . \quad . \quad (50)$$

from which follows:

$$s^3 - 4s(s+2\gamma') + 16\gamma' = 0 \quad . \quad . \quad . \quad (51)$$

hence:

$$\gamma' = \frac{s^2(s-4)}{8(s-2)}; \quad \kappa' = \frac{s^3-8s^2+8s}{12(s-2)} \quad . \quad . \quad . \quad (52)$$

The points of the left-side branch are then given by the values of s between $+\infty$ and 2, those of the right-side branch by the others.

For $s=2$ we get the two infinite branches belonging to the asymptote:

$$2\gamma' - 3\kappa' = 2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (53)$$

19. Nor do we meet with any difficulties in the calculation of the breadth-relations of the regions for very large values of γ' mentioned in § 10.

For the cubic curve we may put:

$$3\kappa' = 2\gamma' + k\sqrt{\gamma'} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (54)$$

through which its equation passes into:

$$(-k^3 + 8k)\sqrt{\gamma'} + 16 - 4k^2 = 0 \quad . \quad . \quad . \quad . \quad (55)$$

from which appears that for very large values of γ' we find $-2\sqrt{2}$, 0 and $+2\sqrt{2}$ for k . We get therefore for the leftside branch of the cubic curve approximately:

$$\kappa' = \frac{2}{3}\gamma' - \frac{2}{3}\sqrt{2} \cdot \sqrt{\gamma'} \quad . \quad . \quad . \quad . \quad . \quad . \quad (56)$$

and for that on the right-side:

$$\kappa' = \frac{2}{3}\gamma' + \frac{2}{3}\sqrt{2} \cdot \sqrt{\gamma'} \quad . \quad . \quad . \quad . \quad . \quad . \quad (57)$$

while of course the middle branch with asymptote corresponds with $k=0$. For this branch we have:

$$\kappa' = \frac{2}{3}\gamma' - \frac{2}{3} \quad . \quad . \quad . \quad . \quad . \quad . \quad (58)$$

In a similar way we find for the parabolic border curve:

$$\kappa' = \frac{2}{3}\gamma' \pm \frac{2}{9}\sqrt{6} \cdot \sqrt{\gamma'} \quad . \quad . \quad . \quad . \quad . \quad . \quad (59)$$

Taking this into consideration we may equate the breadth of the yellow region at infinity to $\frac{2}{9}(3-\sqrt{3})\sqrt{2} \cdot \sqrt{\gamma'}$, that of the green one to $\frac{2}{9}\sqrt{6} \cdot \sqrt{\gamma'}$, that of the blue one to $\frac{2}{3}$, that of the purple one again to $\frac{2}{9}\sqrt{6} \cdot \sqrt{\gamma'}$ and that of the red one to $\frac{2}{9}(3-\sqrt{3})\sqrt{2} \cdot \sqrt{\gamma'}$ from which the relations of equation (9) easily follow, while $\sqrt{3} - 1 = 0.732$.

The spinodal curve.

20. The equation of the spinodal curve is found by elimination of m from (40) and (41). We must, however, take into account, when writing these two equations, that v' along the spinodal curve must be considered to be of the order \sqrt{x} , so that the terms with v'^2 must also be taken into consideration.

We get then:

$$\frac{m}{v_{sp.}} - \frac{3}{4} (2\gamma' - 3\kappa') = 0 \quad . \quad . \quad . \quad . \quad . \quad (60)$$

and

$$-\frac{3}{4} (2\gamma' - 3\kappa') m + \frac{9}{4} t' + \frac{27}{16} v_{sp.}'^2 + \frac{9}{2} (\gamma' - \kappa') x_{sp.} = 0 \quad . \quad (61)$$

from which follows for the equation of the spinodal curve:

$$v_{sp.}'^2 - \frac{1}{3} [(2\gamma' - 3\kappa')^2 - 8(\gamma' - \kappa')] x_{sp.} + \frac{4}{3} t' = 0 \quad . \quad . \quad (62)$$

This is, however, its equation on the ψ' -surface. In order to know it on the original ψ -surface, we must transform it with the aid of (26) into

$$(v_{sp.} - 3b_1)^2 - 3b_1^2 [(2\gamma' - 3\kappa')^2 - 8(\gamma' - \kappa')] x_{sp.} + 12b_1^2 t' = 0. \quad . \quad (63)$$

For that of the circle:

$$(v - 3b_1)^2 + (x - R - \delta)^2 = R^2, \quad (\delta \text{ small})$$

we may write with the same approximation:

$$(v - 3b_1)^2 - 2Rx + 2R\delta = 0,$$

from which we may immediately derive the expression (10) for the radius of curvature of the (v, x) projection of the spinodal curve.

The two first connodal relations. Equation of the connodal curve.

21. We shall now take $P_1(v_1, v'_1)$ and $P_2(v_2, v'_2)$, for which $v'_2 > v'_1$, as denoting two corresponding connodes.

We put then:

$$v'_1 = v'' - \eta; \quad v'_2 = v'' + \eta; \quad x_1 = x'' - \xi\eta; \quad x_2 = x'' + \xi\eta; \quad . \quad (64)$$

hence:

$$v'' = \frac{1}{2} (v'_1 + v'_2); \quad \eta = \frac{1}{2} (v'_2 - v'_1); \quad x'' = \frac{1}{2} (x_1 + x_2); \quad \xi = \frac{x_2 - x_1}{v'_2 - v'_1}; \quad (65)$$

where therefore (v'', x'') indicates a point halfway between the two connodes and ξ denotes the tangent of the angle which the projection on the (v', x) -surface of the join of the connodes forms with the v' -axis.

It is then easy to anticipate, and it is confirmed by the calculations, that all these quantities v'' , x'' and ξ with the exception of η , are of the same order with each other and with t' ; on the contrary not η but η^2 is of this same order.

22. Taking this into consideration the *first* connodal relation:

$$\frac{\partial \psi'_2}{\partial x_2} = \frac{\partial \psi'_1}{\partial x_1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (66)$$

yields at first approximation:

$$\log (x'' + \xi \eta) - \frac{3}{4} (2\gamma' - 3\kappa') (v'' + \eta) = \log (x'' - \xi \eta) - \frac{3}{4} (2\gamma' - 3\kappa') (v'' - \eta) \quad . \quad (67)$$

or also, subtracting on either side $\log x''$:

$$\log \left(1 + \frac{\xi \eta}{x''} \right) - \frac{3}{2} (2\gamma' - 3\kappa') \eta = \log \left(1 - \frac{\xi \eta}{x''} \right) \quad . \quad . \quad (68)$$

or, as $\frac{\xi \eta}{x''}$ is a small quantity of the order of η , we get after development into series and division by η :

$$\xi = \frac{3}{4} (2\gamma' - 3\kappa') x'' \quad . \quad . \quad . \quad . \quad . \quad . \quad (69)$$

in which we shortly point out that this formula passes into formula (46) in the plaitpoint, and further that it leads immediately to formula (24) of the descriptive part.

In the same way the *second*¹⁾ connodal relation:

$$\frac{\partial \psi'_2}{\partial v_2} = \frac{\partial \psi'_1}{\partial v_1}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (70)$$

yields at approximation:

$$\begin{aligned} & -\frac{3}{8} - \frac{3}{2} t' + \frac{9}{4} t' (v'' + \eta) + \frac{9}{16} (v'' + \eta)^3 - \frac{3}{4} (2\gamma' - 3\kappa') (x'' + \xi \eta) + \\ & + \frac{9}{2} (\gamma' - \kappa') (v'' + \eta) x'' = -\frac{3}{8} - \frac{3}{2} t' + \frac{9}{4} t' (v'' - \eta) + \frac{9}{16} (v'' - \eta)^3 - \\ & - \frac{3}{4} (2\gamma' - 3\kappa') (x'' - \xi \eta) + \frac{9}{2} (\gamma' - \kappa') (v'' - \eta) x'', \quad . \quad . \quad . \quad . \quad . \quad . \quad (71) \end{aligned}$$

or, after reduction and division by η :

¹⁾ We must here have recourse to the terms of the order $t'^{\frac{3}{2}}$ or η^3 , as all those of lower order cancel each other. For the sake of clearness we have kept $(v'' + \eta)$ and also $(v'' - \eta)$ together, though it is evident, that we may write e.g. for $(v'' + \eta)^3$ at once η^3 on account of the difference in order of v'' and η .

$$\frac{9}{2} t' + \frac{9}{8} \eta^2 - \frac{3}{2} (2\gamma' - 3\kappa') \xi + 9 (\gamma' - \kappa') x'' = 0, \quad . \quad . \quad (72)$$

from which follows in connection with (69):

$$\eta^2 - [(2\gamma' - 3\kappa')^2 - 8 (\gamma' - \kappa')] x'' + 4 t' = 0. \quad . \quad . \quad (73)$$

23. This formula yields at once the radius of curvature of the (v, x) -projection of the connodal curve. We need only observe that according to definition:

$$v'_{conn.} = v'' \pm \eta; \quad x_{conn.} = x'' \pm \xi \eta; \quad . \quad . \quad . \quad (74)$$

so at first approximation:

$$\eta = \pm v'_{conn.} = \pm \frac{v_{conn.} - 3b_1}{3b_1}; \quad x'' = x_{conn.} \quad . \quad . \quad . \quad (75)$$

Substitution of these last relations in (73) now yields immediately the equation of the connodal curve and in exactly the same way as for the spinodal curve we find from it the value of the radius of curvature $R_{conn.}$ given in formula (11). A further explanation of the way in which the knowledge of this value leads to the formulae (13) and (14) need not be given here, nor need we explain the derivation of the formulae (18) and (19), (21) and (22).

But the derivation of formula (20) will detain us for a moment; we require, namely, for it a more accurate expression for p than that given in formula (23). If we therefore develop (31) as far as needful for the purpose, we find ¹⁾:

$$p = -\frac{8}{3} p_k \left(-\frac{3}{8} - \frac{3}{2} t' + \frac{9}{4} t' v' - \frac{3}{4} (2\gamma' - 3\kappa') x + \frac{9}{2} (\gamma' - \kappa') v' x \right), \quad (76)$$

or:

$$\frac{p - p_k}{p_k} = 4 t' - 6 t' v' + 2 (2\gamma' - 3\kappa') x - 12 (\gamma' - \kappa') v' x, \quad . \quad (77)$$

thence:

$$\frac{p_P - p_R}{p_k} = -6 t' (v'_P - v'_R) + 2 (2\gamma' - 3\kappa') (x_P - x_R) - 12 (\gamma' - \kappa') (v'_P - v'_R) x_P, \quad (78)$$

for, with regard to the last term, the difference of x_P and x_R is slight compared to that between v'_P and v'_R .

¹⁾ It might appear as if $\frac{9}{16} v'^3$ ought also to be inserted in the following expression, but it is easy to see that this term leads to a small quantity of higher order than those that will occur in the final result.

It is now easy to find :

$$x_P - x_R = \frac{1}{2} m (v'_P - v'_R) = \frac{3}{8} (2\gamma' - 3\kappa') x_P (v'_P - v'_R), \quad (79)$$

either by paying attention to the fact that we have in Fig. *d*, § 12 (see the first descriptive part), if applied to the (v', x) -diagram, with a sufficient degree of approximation :

$$RQ = PQ \cdot tg RPQ = PQ \cdot tg \frac{1}{2} \mu = \frac{1}{2} \cdot PQ \cdot tg \mu = \frac{1}{2} \cdot PQ \cdot m,$$

or by application of the formulae (13) and (14), observing that $v_P - v_R = 3b_1 (v'_P - v'_R)$.

This yields by substitution in (78) :

$$\frac{p_P - p_R}{p_k} = \left(-6t' + \frac{3}{4} (2\gamma' - 3\kappa')^2 x_P - 12(\gamma' - \kappa') v_P \right) (v'_P - v'_R), \quad (80)$$

or finally substituting for t' its value from (47)

$$\frac{p_P - p_R}{p_k} = -\frac{3}{4} (2\gamma' - 3\kappa')^2 x_P (v'_P - v'_R) = -\frac{1}{4b_1} (2\gamma' - 3\kappa')^2 x_P (v_P - v_R), \quad (81)$$

from which we immediately derive formula (20), applying (18).

The third connodal relation.

24. We have now obtained the principal formulae. For the sake of completeness, however, we shall treat here also the third connodal relation, the more so as this leads to a new determination of the formulae (47) and (48), which puts the former to the test.

This third relation reads :

$$\psi'_2 - x_2 \frac{\partial \psi'_2}{\partial x_2} - v'_2 \frac{\partial \psi'_2}{\partial v'_2} = \psi'_1 - x_1 \frac{\partial \psi'_1}{\partial x_1} - v'_1 \frac{\partial \psi'_1}{\partial v'_1}. \quad (82)$$

We first transform $\psi' - x \frac{\partial \psi'}{\partial x} - v' \frac{\partial \psi'}{\partial v'}$, with the aid of (32). It proves to be necessary to keep all terms up to the order $t^{\frac{5}{2}}$ or η^5 . So we find :

$$\psi' - \frac{\partial \psi'}{\partial x} - v' \frac{\partial \psi'}{\partial v'} = -(1+t')v + \chi_0 - v' \frac{\partial \chi_0}{\partial v'} - v' x \frac{\partial \chi_1}{\partial v'} - \left(\chi_2 + v' \frac{\partial \chi_2}{\partial v'} \right) v^2. \quad (83)$$

From this follows :

$$\begin{aligned} \psi'_2 - x_2 \frac{\partial \psi'_2}{\partial x_2} - v'_2 \frac{\partial \psi'_2}{\partial v'_2} = & -(1+t')(x'' + \xi\eta) - (1+t') \log 2b_1 - \frac{9}{8} - \frac{9}{8} t' (\eta^2 + 2v''\eta) + \\ & + \frac{9}{4} t' \eta^3 - \frac{27}{64} (\eta^4 + 4v''\eta^3) + \frac{63}{40} \eta^5 + \frac{3}{4} [(2\gamma' - 3\kappa') + 2\gamma' t'] (\eta + v'') (x'' + \xi\eta) - \\ & - \frac{9}{2} (\gamma' - \kappa') (\eta^2 + 2v''\eta) (x'' + \xi\eta) + \frac{27}{8} (3\gamma' - 2\kappa') \eta^3 x'' - \sigma_0 (v''^2 + 2x''\xi\eta) - 2\sigma_2 \eta v''^2. \end{aligned} \quad (84)$$

If we equate this to the corresponding expression for

$$\psi_1 - x_1 \frac{\partial \psi_1}{\partial x_1} - v_1 \frac{\partial \psi_1}{\partial v_1},$$

which is obtained by changing η into $-\eta$, we get, dividing by η :

$$\begin{aligned} & -2\xi - 2t'\xi - \frac{9}{2}t'v'' + \frac{9}{2}t'\eta^2 - \frac{27}{8}v''\eta^2 + \frac{63}{20}\eta^4 + \frac{3}{2}(2\gamma' - 3\kappa')x'' + 3\gamma'tx'' + \\ & + \frac{3}{2}(2\gamma' - 3\kappa')v''\xi - 9(\gamma' - \kappa')\xi\eta^2 - 18(\gamma' - \kappa')v''x'' + \\ & + \frac{27}{4}(3\gamma' - 2\kappa')\eta^2x'' - 4\sigma_0x''\xi - 4\sigma_2x''^2 = 0. \quad \dots \quad (85) \end{aligned}$$

At first approximation this yields:

$$\xi = \frac{3}{4}(2\gamma' - 3\kappa')x''.$$

This relation is, however, identical with the relation (69) which is derived from the first connodal relation. So we cannot draw any further conclusion from equation (85) without bringing it into connection with the first connodal relation; but for this it is required to introduce a further approximation for the latter.

Second approximation of the first connodal relation.

25. From the first connodal relation in connection with the equation

$$\frac{\partial \psi'}{\partial x} = 1 + t' + (1 + t') \log x + \chi_1 + 2\chi_2x + \dots \quad \dots \quad (86)$$

the following relation may easily be derived, if we take into account the terms up to the order t'^3 or η^3 :

$$\begin{aligned} & (1 + t') \log \frac{1 + \frac{\xi\eta}{x''}}{1 - \frac{\xi\eta}{x''}} - \frac{3}{2}(2\gamma' - 3\kappa')\eta - 3\gamma'\eta t' + 9(\gamma' - \kappa')v''\eta - \frac{9}{4}(3\gamma' - 2\kappa')\eta^3 + \\ & + 4\sigma_0\xi\eta + 4\sigma_2\eta x'' = 0 \quad \dots \quad (87) \end{aligned}$$

Within the same order of approximation we have however:

$$\log \frac{1 + \frac{\xi\eta}{x''}}{1 - \frac{\xi\eta}{x''}} = \frac{2\xi\eta}{x''} + \frac{2\xi^3\eta^3}{3x''^3}.$$

In the second term of the second member of this equation, however, we may safely make use of the first approximation furnished by equation (69). Taking this into account (87) passes after multiplication with x'' and division by η into:

$$2\tilde{\xi} + 2\tilde{\xi}t' + \frac{9}{32}(2\gamma' - 3\kappa')^3\eta^2x'' - \frac{3}{2}(2\gamma' - 3\kappa')x'' - 3\gamma'x''t' + 9(\gamma' - \kappa')v''x'' - \\ - \frac{9}{4}(3\gamma' - 2\kappa')\eta^2x'' + 4\sigma_6\tilde{\xi}x'' + 4\sigma_2x''^2 = 0. \quad (88)$$

Further reduction of the third connodal relation.

Derivation of equation (25) of the first descriptive part.

26. By addition of (85) and (88) we find: ¹⁾

$$-\frac{9}{2}t'v'' + \frac{9}{2}t'\eta^2 - \frac{27}{8}v''\eta^2 + \frac{63}{20}\eta^4 - 9(\gamma' - \kappa')\tilde{\xi}\eta^2 - 9(\gamma' - \kappa')v''x'' + \\ + \frac{3}{2}(2\gamma' - 3\kappa')v''\tilde{\xi} + \frac{9}{32}[(2\gamma' - 3\kappa')^3 + 16(3\gamma' - 2\kappa')]\eta^2x'' = 0. \quad (89)$$

When we add to this relation (72), which is deduced from the second connodal relation, after having multiplied it with v'' , we can divide by η^2 and we get:

$$\frac{9}{2}t' - \frac{9}{4}v'' + \frac{63}{20}\eta^2 - 9(\gamma' - \kappa')\tilde{\xi} + \frac{9}{32}[(2\gamma' - 3\kappa')^3 + 16(3\gamma' - 2\kappa')]\eta^2x'' = 0. \quad (90)$$

Making use of (69) we may solve the quantity v'' from this equation:

$$v'' = 2t' + \frac{7}{5}\eta^2 + \frac{1}{8}[(2\gamma' - 3\kappa')^3 - 24(2\gamma' - 3\kappa')(\gamma' - \kappa') + 16(3\gamma' - 2\kappa')]\eta^2x'', \quad (91)$$

or finally with the aid of (73):

$$v'' = -\frac{18}{5}t' + \left\{ \frac{7}{5}[(2\gamma' - 3\kappa')^2 - 8(\gamma' - \kappa')] + \right. \\ \left. + \frac{1}{8}[(2\gamma' - 3\kappa')^3 - 24(2\gamma' - 3\kappa')(\gamma' - \kappa') + 16(3\gamma' - 2\kappa')]\right\}x''. \quad (92)$$

from which equation (25) follows immediately with the aid of (65) and (26).

In this way we have found the starting-point of the curve in the (v, x) -diagram described by the point halfway between the points which represent coexisting phases. The tangent in that starting point also is now known.

¹⁾ Remarkable is the disappearance of the terms derived from $x_2 x^2$, which makes also λ' and ϑ' , i. e. $\frac{a_2}{a_1}$ and $\frac{b_2}{b_1}$ disappear from the result. We have tested the truth of this in different ways.

*A new determination of the plaitpoint, independent
of the preceding one.*

27. It is now easy to obtain such a determination with the aid of (73) and (91). For in the plaitpoint we have:

$$\eta = 0 \quad ; \quad x'' = x_P \quad ; \quad v'' = v'_P.$$

From (73) follows immediately (47); from (91):

$$v'_P = 2t' + \frac{1}{8} [(2\gamma' - 3\kappa')^3 - 24(2\gamma' - 3\kappa')(\gamma' - \kappa') + 16(3\gamma' - 2\kappa')]x_P; \quad . \quad (93)$$

from which in connection with (47) we find again (48).

Physics. — “*Some remarkable phenomena, concerning the electric circuit in electrolytes*”. By Mr. A. H. SIRKS. (Communicated by Prof. H. A. LORENTZ).

On etching of metal-alloys by means of the electric current, as communicated in the proceedings of the meeting of September 27, 1902, I met with a great difficulty. In some cases the hydrogen developed at the kathode was very troublesome, namely when, instead of escaping immediately it divided itself in small bubbles through the liquid and stuck to the object to be etched used as anode. This obstacle was overcome by surrounding the kathode with fine brass-gauze, so that the gasbubbles were compelled to escape directly in this case. The gauze was hung up apart, consequently there was no contact, whatever, with one of the electrodes. The etching being finished, copper proved to have been precipitated on the wires of the gauze, which deposit was almost conform to the shape of the electrodes.

This was still more visible at a second etching-experiment with the same copper-alloy: a small cup was placed under the anode, which partly hung in it. Again on the gauze a copper-deposit was perceptible, which showed at the lower side a distinctly designed horizontal margin, nearly as high as the brim of the cup.

It was to be expected, that copper should precipitate on the gauze, placed between the electrodes, as the whole apparatus can be considered as two voltmeters, connected in series¹⁾. But, why is by this electrolysis not the whole side of the gauze, facing the anode, coppered, as is the case with the kathode by any ordinary electrolysis?

To answer this question the experiments were altered somewhat.

¹⁾ The anode and the side of the gauze facing it, are the electrodes of one, the other side of it and the kathode, those of the other voltmeter.

Instead of water acidulated with sulphuric-acid a saturated solution of copper-sulphate was used as electrolyte; the electrodes were formed in future by two equally large Dutch bronze coins. The back part of these coins and the battery-wires, to which they were soldered, were varnished, as far as they were immersed in the electrolyte, in order to be sure, that, during the electrolysis, the facing-sides only served as pole-plates. The gauze tube was left away and a screen of platinum (4×4 c.m.), hung up isolated, placed just amidst the electrodes, who were 4 c. m. from each other. If a copper-deposit might appear on the platinum, this could be ascribed to electrolytic actions only. Very soon after the circuit was closed (intensity ± 0.3 amp; voltage of the battery = 4 volts) there came on the piece of platinum facing the anode a sharply bounded copper-deposit, which, by continuation of the experiment, changed of thickness exclusively and not of size. The experiment was continued for 2 days; still the results remained the same.

Now I resolved to remove the platinum screen between the electrodes, to do the experiment over again and repeat this several times. The deposits obtained in all these cases were not exactly of the same size. The smallest deposit (diam. 18 mM) was obtained by hanging the screen between the electrodes (diam. 19 mM.), from which we can conclude to a small gradual contraction to the middle.

If two electrodes of different shape were used, then, by removing the platinum screen from the anode to the kathode, the copper-deposit passed from the shape of one electrode into that of the other. This was very clearly visible by using a nut as anode and a square piece of sheet-copper as kathode. The hexagonal copperdeposit gradually took a square shape.

Superficially one would be inclined to suppose, that the only thing, that has happened is the locally making of sections of the envelope of the two electrodes by means of the screen, but considering, that, if electricity passes from one electrode to the other, the stream-lines divide through the whole fluid — the current-density is only larger within the above-mentioned envelope — it will be obvious, that there must have been another cause, which made some stream-lines prefer to take the way round the screen to the shorter one through it. Considering, that the resistance of the platinum can be neglected in regard to that of the longer way through the fluid, the explanation of the deviation of these stream-lines can only be found in the polarisation, caused by the screen of platinum.

To prove the supposal, that stream-lines are going out from the electrodes in all directions, the following experiment may serve: The

anode was hung in a platinum cup, which must replace the platinum diaphragm and was therefore partly filled with the electrolyte. Directly the circuit was closed, the inside of the cup was evenly coppered, as high as the surface of the liquid, while at the outside an intense gas-development took place, which was soon impossible to be observed well, as on account of the polarisation the current-intensity was considerably decreasing. In some cases from 0,9 amp. to 0,02 amp. If on the reverse the kathode was hung in the cup, the development of gas took place at the whole inside. Half of the outside of the cup facing the anode was partly and unevenly covered with a copper-deposit.

When making the experiment with a sheet of platinum (5×5 cm.), dividing the glass in two equal parts, the results were just the same. Here also the platinum was entirely covered with precipitated copper. At a distance of the electrodes of about 10 m.m., the copper-deposit was pretty evenly spread over the platinum. At a smaller distance of the electrodes (4 m.m.) there came between the electrodes on the platinum a distinct circular deposit, while the copper precipitated on the remainder of the screen was very faint. A same deposit perfectly corresponds with the sections of the stream-lines we should expect.

The same results were obtained, when using two diaphragms dividing the cup into three parts. At the first experiment two diaphragms were used, completely shutting off the fluid and connected with a copper-wire. The side of the first diaphragm, facing the anode, counting from the anode to the kathode, was entirely coppered; the side of the other one, facing the kathode, was covered with gas-bubbles.

At a second experiment only the connecting wire was taken away. The sides of both diaphragms, facing the positive electrode, were entirely covered with a copper-deposit. On the other sides gas was developing.

At a third experiment two platinum screens (4×4 cm.) were used, thus not shutting off the fluid completely, but connected, however, with a copper-wire. The same circular copper-deposit came on the first screen, facing the anode, but, when breaking the connection the same side of the second screen was, on the contrary, entirely covered with copper.

The latter phenomenon can be explained in this manner: The copper-ions, leaving the anode, yielded their charge to the first screen, over which it is entirely distributed and which, over the whole side, facing the kathode, serves in its turn as anode towards the second screen, which is coppered over the whole surface. If the second

screen was larger than the first, then, the side of the former, facing the anode, was coppered for a part about as large as the latter.

Then, the experiment was repeated with a screen, dividing the basin into two equal parts, but having a small hole in the middle. Just as a part of the stream-lines in some of the former experiments went round the screen, so here a very great contraction of the stream-lines towards the hole may be expected. Some of them will deviate from their straight way preferring the way through the hole, to the way through the screen. This is confirmed by a circular part of the screen remaining uncovered.

The following data are the results of a series of experiments, taken with holes of different size.

Diameter of the hole.		Diameter of the uncovered part.
1 mm.		7 mm.
2 "		10 "
4 "		14 "
5 "		17 "
8 "		25 "
15 "		whole screen uncovered.

distance between electrodes 3 cm., diameter of electrodes 19 mm.

If the smaller screen is taken, so that stream-lines can also go round it as well, then the uncovered part is considerably smaller. The diameter of it was 3 mm. at a 1 mm. diameter of the hole.

It is worth notice, that, while the electro-motive force remained the same, the current-intensity increased on increasing the diameter of the aperture. If for instance at the experiment with the smallest hole (diam. 1 mm.) the intensity after the beginning of the polarisation was 0,1 amp., it amounts under the same circumstances to 0,3 amp., when using the screen with the biggest hole.

It is curious, that at the first experiment a copper-deposit was seen on the case of brass gauze surrounding the kathode, though properly it is nothing but a screen with a great number of small holes. According to what is said before, it might have been expected, that all the stream-lines would pass from the anode through the holes of the case to the kathode and therefore not form any deposit on the gauze. In connection with this, some more experiments were taken with different sorts of brass gauze, but already by using the next size — stitches of 2 mm² and 0,3 mm. wires — no traces of copper were precipitated.

If the way through the fluid was made considerably longer, then, in some cases, the current still seemed to prefer this round-

about way to the undoubtedly shorter one through the screen. This was done in the following way: Again the anode was hung in a platinum cup, over the brim of which hung a bent glass-tube, filled with the copper-sulphate solution, thus forming the connection between the electrolyte at the inner- and outer side of the cup. Even if a capillary tube was used, a deviation was observed in the copper-deposit, namely: a part of the cup near the lower end of the tube was not coppered, this, however, only when the tube was hung over that place on the brim of the cup between the electrodes. A 3 mm. tube, however, caused a deviation of the deposit, even, if the tube was hung over the brim of the cup on the prolongation of the centre-line of the electrodes.

Of course, there must be some relation between the coppering of the inner surface of the cup in these cases and the circular deposit on the screen. It must be possible, therefore, to pass gradually from one deposit into the other. Instead of the cup a cylinder of platinum, having a diameter of 4 cm., was used, which at the bottom was melted in a basin with paraffine and projected from the fluid. The anode was hung in it again. The circuit being closed, the inside of the cylinder was of course coppered again as far as it was immersed in the electrolyte (50 mm.). Then a vertical cleft of 1 mm. wide and 1 mm. high was made in the cylinder on the extension-line of the centres of electrodes. A part of the inner wall round the cleft remained again uncovered. When gradually giving the cleft a height of 20 mm., the uncovered part took the form of an ellipse, till at a height of 25 mm. a strip of 8 mm. wideness was not covered with copper, along the whole height, i. e. 50 mm., of the electrolyte. When still enlarging the cleft, the deposit gradually receded more from the margins and after unfolding the cylinder into a plane it finally took the already known circular form again.

To make the explanation, given of the deviation of the stream-lines on account of the polarisation of the platinum, more acceptable, the experiments were made with different electromotive forces by inserting resistance. By means of a resistance box, connected parallel with the voltmeter, the terminal voltage of the latter could be increased. The current-intensity could be read on a milli-amperemeter, joined in circuit with the voltmeter. As long as the potential difference was less than the electro-motive force of the polarisation, nothing was precipitated. After more resistance had been inserted in the resistance box, a current began to pass through the voltmeter, but without forming a deposit on the sheet of platinum, although the experiment was carried on some hours. For that reason this current

could not have chosen its way through the screen and must have gone therefore round it. If some more resistance was inserted, then a deposit came gradually on the screen, smaller and more uneven than in the ordinary case, but also taking the normal size and thickness as formerly, when going on inserting more resistance.

Different salts were used as electrolyte, in none however, a deposit was so easily formed as in cupric sulphate. The phenomenon, when using this salt, was so clear, that once a deviation in the shape of the deposit was observed, because the wire which was connected to the anode, was not sufficiently insulated. In saturated solutions of zinc-, aluminium-, nickel-, cobalt-, ferrous- and ferric sulphate deposits were formed, one clearer than the other even if in all these cases the constant current-intensity was secured by inserting resistance.

Chlorides were also used as electrolytes. In chlorides of zinc and cadmium exactly the same circular deposit was formed, but in those metals, which can form more than one chloride (e.g. iron), a secondary phenomenon always appeared. When a solution of cupric-chloride was electrolysed, copper precipitated on the kathode; when, however, a platinum screen was put between the electrodes, again a circular deposit of a white substance was formed on the screen, quickly getting green in the air and being hygroscopic then; probably it might have been cuprous chloride, afterwards becoming cupric chloride again. When using a solution of Hg Cl_2 as electrolyte a white deposit of Hg Cl came on the platinum. A solution of Au Cl_3 gave conformable results; a brown red deposit was formed. Using $\text{H}_2 \text{ Pt Cl}_6$ and a screen of gold-leaf, a yellow brown one was formed on the latter. When a solution of ferric chloride was used no deposit was ever formed. The explanation may be found perhaps in the solubility of ferrous chloride which is precipitated on the platinum as copper before.

Though in many of the former cases an explanation could be found in the polarisation, yet, however, there is one thing, that cannot be explained, i. e. the curious sharp margins of the deposit. It seems as if the stream-lines keep their original direction within a certain tubular surface also in the presence of the platinum screen, while this screen has a strong influence on the lines outside of it, which change their direction and go round the screen. Perhaps the explanation may be found by calculating the course of the circuit, but I am not able to do it.

In the making of all these experiments I have become indebted

to professor ARONSTEIN and professor SCHROEDER VAN DER KOLK for their assistance of various kinds and to these I tender my best thanks. Also to Professor H. A. LORENTZ, professor at the Leyden University, for his help and information.

Mineralogical Laboratory.

Polyt. School.

Delft, Jan. 1903.

(February 25, 1903).

KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN TE AMSTERDAM.

PROCEEDINGS OF THE MEETING of Saturday February 28, 1903.

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The following papers were read:

Physics. — "*Critical phenomena of partially miscible liquids — ethane
and methylalcohol.*" By J. P. KUENEN. (Communicated by
Prof. H. KAMERLINGH ONNES).

(Communicated in the Meeting of September 27, 1902).

Some years ago Mr. W. G. ROBSON and I began a systematic
investigation of the phenomena of condensation for mixtures of liquids
which do not mix in all proportions ¹⁾. Shortly afterwards Prof. van
DER WAALS communicated to this Society an important paper in which
he discussed our results ²⁾ and again in the second volume of his
treatise on the Continuity ³⁾ he devotes some pages to the conside-

¹⁾ Zeitschrift für Physik. Chemie 28, p. 342—365. Phil. Mag. (5) 48, p. 180—203.

²⁾ Kon. Ak. van Wet. Amsterdam 25th March 1899.

³⁾ Die Continuität etc. II. 1900, p. 184—192.

ration of the same phenomena. After the publication of Prof. VAN DER WAALS'S paper I approached him privately with some objections to his views to which he replied in the most courteous manner. Though not completely satisfied it seemed unnecessary at the time to publish my views until I should be in a position to add to our knowledge of the phenomena by further experiments.

I have recently resumed the investigation and the results obtained, though naturally far from complete, seem of sufficient importance to deserve an immediate publication and to be discussed in connection with previous experiments.

For various reasons we had fixed our choice on mixtures of hydrocarbons — first of all ethane — and alcohols. Briefly our results were as follows:

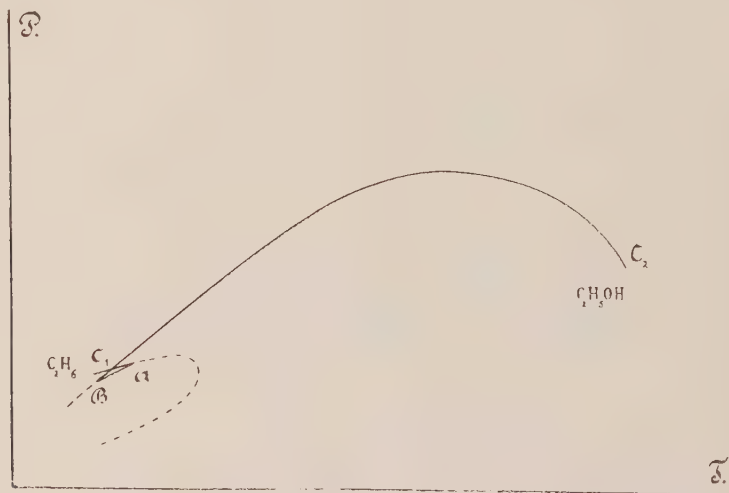


Fig 1.

For mixtures of ethane with ethyl-, propyl-, isopropyl- and butyl-alcohol there are two temperatures *A* and *B* (Fig. 1) between which three phases — two liquids and vapour — are possible and the critical (i.e. plaitpoint) curve accordingly consists of two branches, C_1A and C_2B , C_1 and C_2 representing the critical points of ethane and alcohol respectively and AB the three-phase curve. For ethyl-alcohol *A* and *B* are comparatively far apart; for the higher terms of the series these points gradually approach each other and with amylalcohol no separation into two liquids could be observed; in this case the critical curve was a continuous curve joining the two critical points C_1 and C_2 in the usual manner.

For mixtures of methylalcohol and ethane we found a branch C_1A

and a three-phase curve ending at A , as with the higher alcohols, but not a limit B below which the liquids mix in all proportions. The character of the other branch of the critical curve which begins at C_2 , the critical point of methylalcohol, therefore remained uncertain.

Prof. VAN DER WAALS's remarks concerned firstly the explanation of the behaviour of the first group of mixtures and secondly of the different behaviour of methylalcohol and the prediction of the phenomena outside the limits of our researches. The experiments communicated in this paper have reference to the latter problem.

First of all Prof. VAN DER WAALS shows how the two branches C_1A and C_2B may be made into one continuous curve by producing them in the region of the metastable and unstable conditions, a region which I shall call the "theoretical" region. In our paper we had pointed out that the phenomena were completely explained by the formation of a new subsidiary plait with plaitpoint emerging out of the main plait on the ψ -surface and the subsequent withdrawal and disappearance of the main plaitpoint¹⁾. Having regard to VAN DER WAALS's original investigation and to KORTEWEG's treatise²⁾ on the properties of the ψ -surface, the simplest interpretation appears to be to assume that at some temperature higher than T_A a closed plait begins to develop on the spinodal curve, increasing in extent as the temperature falls, until one of its plaitpoints — that of the first kind³⁾ — at A pierces the connodal curve of the main plait, thus giving rise to the formation of the subsidiary plait and the three-phase triangle. On further fall of temperature the inner plaitpoint exchanges partners, so as to form a closed plait with that branch of the main plait on which the original plaitpoint lies: at B the connodal curve of the main plait begins to enclose this closed plait. We may moreover assume the latter to contract on further cooling and ultimately shrink to nothing⁴⁾. Transferring the above changes to the p - t -diagram we obtain the figure deduced from ours by Prof. VAN DER WAALS.

1) l. c. p. 358—359.

2) Arch. Néerl. 24 p. 295—368 in particular p. 316 etc.

3) Comp. KORTEWEG p. 67.

4) Whether this actually takes place seems at least doubtful. The *formation* of the plait on cooling is hardly open to doubt, seeing that at high temperatures the ψ -surface cannot show any abnormalities in the region under consideration: but this condition does not hold at low temperatures and the contraction of a closed plait on cooling is in contradiction with the rule enunciated by Prof. VAN DER WAALS regarding the influence of temperature on the extension of plaits.

The possibility of producing the theoretical curves in the p - t -diagram had escaped our notice ¹⁾.

In the first place Prof. VAN DER WAALS observes that the completed figure is in contradiction with the law previously deduced by him ²⁾ that a mixture of non associating substances may have a maximum or minimum critical temperature, but not both. To this point one of my objections refers. The law depends entirely on the simple characteristic equation, but apart from that it only refers to the critical point of the homogeneous mixtures and it must be looked upon as a possibility that the curve of the critical points — the plaitpoints — should have both a maximum and a minimum. Prof. VAN DER WAALS replies to this ³⁾ that near a maximum or minimum the two curves in question are so close to each other that no such difference between them can be admitted. This argument does not satisfy me. The two curves touch each other at points where a maximum or minimum *vapour pressure* exists and the two phases have the same composition, but points of that kind do not exist in the case under consideration. It is true that a maximum or minimum occurs on the plait when the connodal curve intersects the spinodal curve, but the character of these points is entirely different from that of the points referred to. The three-phase pressure for mixtures of ethane and the alcohol is between the vapour pressures of the components and there is thus no occasion for assuming the existence of another maximum or minimum. That being the case, there is no reason for a close resemblance between the two curves nor any

¹⁾ Note added to translation.

The above was written by me in the conviction which I then held that Prof. VAN DER WAALS's views of the formation of the new plait — although arrived at in a different way — still agreed essentially with my own: indeed I do not even now see, how else the phenomena could be interpreted. From the paper contributed by him in the October-meeting of this society (critical phenomena of partially miscible liquids. Kon. Ak. van Wet. Amst. 25th Oct. 1902) it appears that such was not the case and that I ought to have been more careful in accepting the theoretical curve drawn by him as corresponding to the changes on the \downarrow -surface as understood by myself. Doubt never arose in my mind on this point at all and I never considered the question. Still I ought to have noticed that the theoretical curve has no vertical tangent at its extreme points, but ends in cusps, corresponding to the circumstance that the curvature of the connodal curve is the same in both plaitpoints of the closed plait. This is the only respect in which I think my paper requires emendation although some of my arguments would have been presented in a different manner had I realised how completely his views differed from mine.

²⁾ Arch. Néerl. 24 p. 23.

³⁾ Continuität II p. 188 l. 17.

ground why the "homogeneous" critical curve should have a loop as well as the plaitpointcurve.

I am strengthened in this opinion by the fact, that even in the "symmetrical" case Prof. KORTEWEG has come across similar peculiarities in the plait and it follows, that theoretically even those mixtures which obey VAN DER WAALS's equation may have a critical curve with a loop in it.

I do not mean to maintain that the homogeneous curve in our case does not possess a loop or to deny the probability of Prof. VAN DER WAALS's hypothesis according to which the association of the alcohols plays a part in producing the abnormality. What I want to point out is that it has not been proved that with normal mixtures the abnormality cannot occur, although it is very probable that this abnormality and in general the formation of two liquid layers -- while theoretically possible for normal mixtures with special values of the constants -- in reality occurs with associating substances only¹⁾.

The critical curve in the p, t -diagram having been completed in the way described one feels inclined to say with Prof. VAN DER WAALS that the case is one of a modified cross-plait and not of a true liquid-plait. According to VAN DER LEE's experiments²⁾ the liquid-plait for mixtures of phenol and water has its plaitpoints turned in the direction of the positive volume-axis and above a certain temperature is entirely independent of the cross-plait. Prof. VAN DER WAALS seems inclined to look upon those properties as characteristic of the liquid-plait and to withhold this name from that part of the plait which in our case is turned towards the x -axis. It will appear presently that this view cannot very well be sustained so that at any rate this ground for drawing the distinction in question disappears. Still the peculiarity remains³⁾ that the critical curve is a continuous curve, at least when no account is taken of the objection urged above against joining the curves beyond B . Even then however it will be observed that on the ψ -surface two independent plaits exist completely or partly inside each other and thus when the ψ -surface itself is considered the contrast between our case and one in which a true liquid plait would exist disappears. Moreover the abnormality is ascribed to the same cause -- association -- as the formation of the liquid plait; if both are due to the same cause, one feels even less inclined to maintain a distinction in the nomenclature.

1) Continuität II p. 176. I doubt the possibility of deducing a relation between a_{12} on the one side and a_{11} and a_{22} on the other.

2) Zeitschr. Physik. Chemie, 33, p. 622, 630.

3) Continuität II p. 188.

The following may be added in further explanation: there is a well defined contrast between the two plaits as regards the causes of their existence. The cross-plait depends for its existence on the shape of the ψ -curves for the separate homogeneous mixtures, the liquid-plait on the other hand is due to the manner in which these curves change with the composition. In the formation of the latter plait association seems to be the principal factor. But notwithstanding this distinct contrast there must be a number of cases in which it will be impossible to say which kind of plait one is dealing with and to which sort of plait a given plaitpoint belongs. We shall presently come across a striking instance of this kind where a cross-plait with its plaitpoint gradually changes into a plait with its plaitpoint turned towards the x -axis from which it is impossible to withhold the name liquid-plate.

Let us now consider the case of methylalcohol and ethane. Before communicating the new results I will discuss Prof. VAN DER WAALS's views of these mixtures. He assumes that the critical curve is again a continuous one but with a loop turned upwards this time instead of downwards as with the higher terms.¹⁾ There are some serious objections to this theory:

The critical curve, starting at the critical point of ethane C_1 , disappears from the practical part of the surface at A , as in the former case, and the part beyond can therefore only represent a theoretical plaitpoint which remains hidden, because at higher temperatures no three phases coexist. Beyond A the curve should therefore be dotted throughout, and it cannot be interpreted as in part real. In this case as in the other the shape of the curve was deduced by keeping in view the homogeneous critical point and a striking instance is afforded of how this curve does not give us any clue as to the shape of the real critical curve.

In the second place I think the bending upwards of the critical curve assumed in this case is open to doubt. At somewhat high temperatures there is probably no abnormality on the surface and no plait except the cross-plait: as the temperature falls a closed curve develops one of whose plaitpoints pierces the main plait at A and moves from there towards C_1 . As in the other mixtures the three-phase pressure is lower than the vapour pressure of ethane; it follows that the subsidiary plaitpoint is turned towards the x -axis and represents a maximum pressure on the closed plait. This being so the simplest supposition to make is that the other plaitpoint of

¹⁾ Comp. his diagram Kon. Ak. v. Wetensch. Amst. March 25th, 1899 p. 5.

this closed plait is one of minimum pressure: starting from this point the pressure on this plait passes through a maximum and a minimum successively and reaches its highest value in the real plait-point. In other words the theoretical part of the bent critical curve in the p, t -diagram should lie below the practical part, as with the other alcohols. This supposition seems so much simpler than the opposite one that I feel prompted to state the following rule: *when the three-phase pressure is between the vapour pressures of the components the theoretical critical curve bends downwards, when it is higher than the vapour pressures of the components (as with ether and water¹⁾) the curve bends upwards.*

In his book on the "Continuity"²⁾ the author discusses the probable behaviour of the mixtures at higher temperatures. Apart from a possible plaitpoint on the side of the small volumes on the liquid-plait, there is no practical plaitpoint left above A . Prof. VAN DER WAALS assumes that this condition will continue up to the critical point of methylalcohol, that the plait will close itself here, gradually contract and ultimately disappear either at the limiting liquid-volume or by its plaitpoint meeting with a possible liquid plaitpoint.

This expectation has not been realised by my experiments and must in itself be looked upon as improbable. The formation of the liquid-plait is ascribed to the association of methylalcohol. Above a certain temperature this abnormality has disappeared and in any case at the critical point it is for most substances very small. Considering the great difference between the critical temperatures of the two constituents of the mixture an admixture of ethane to methylalcohol cannot but lower the critical point, even if the mutual attraction of the components were comparatively great. As a matter of fact methylalcohol seems to have some association left at the critical point³⁾. But this association has the effect of making the mutual attraction appear even smaller and thus increases the probability of a lowering of the critical temperature by the addition of ethane. It follows that the cross-plait has to appear on the ψ -surface in the usual manner with fall of temperature, with its plaitpoint turned towards the ethane side.

In view of the fact that at low temperatures there is a liquid-

¹⁾ KUENEN and ROBSON l. c. p. 351.

²⁾ Continuität II, p. 189 verv.

³⁾ RAMSAY & SHIELDS, Zeitschr. Physik. Chemie 15, p. 115. Nobody seems to have observed as far as I know that the comparatively high value of the critical temperature of methylalcohol may be explained by association, as also the deviation from KOPP's law for the boiling points of series of organic substances.

plait there are still two possibilities with regard to the development of this cross-plait: (1) the plaitpoint continues by itself and gradually begins to form the closing plaitpoint of the liquid-plait which may disappear at the limiting liquid volume or (2) it disappears by meeting with a second plaitpoint belonging to an independent liquid-plait so that the two plaits then form one large one, with or without a closing plaitpoint on the liquid side.

The experiments confirm the above view of the effect of an admixture of ethane on the critical point of methylalcohol and as far as they go seem to show the first alternative to be the correct one. It appears that the general behaviour of mixtures of methylalcohol and ethane thus disclosed agrees with that of ether and water as predicted — without however any grounds being given — by KORTEWEG ²⁾ and laid down in some *x-v*-diagrams. On the grounds set forth above I support this expectation as regards ether and water. *Addition of ether to water will lower the critical temperature.*

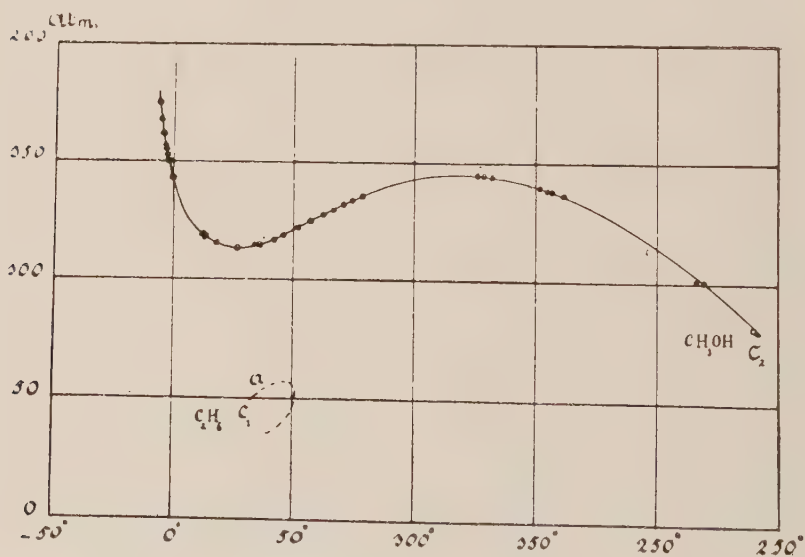


Fig. 2.

The results for methylalcohol and ethane are laid down in figure 2. I can give only a short explanation here. Starting from C'_2 — the critical point of methylalcohol — the critical curve runs in a perfectly normal way at first, owing to the influence of the association being as yet insufficient. It ascends, passes through a maximum at 120° , and then falls, evidently tending towards the critical point

²⁾ Arch. Néerl. 24 p. 338—340.

of ethane; the association however becomes gradually stronger; the dip in the surface caused by this¹⁾ gradually modifies the shape of the cross-plait: the plaitpoint passes through a minimum pressure between 25° and 30° , and the critical curve then begins to rise rapidly. The end of the cross-plait thus changes without a discontinuity into a liquid-plait; in the mean time the main plait goes on developing on the approach of the critical point of ethane: as explained a small subsidiary plait is formed which appears at *A* on the practical part of the surface. Probably an exchange of plaitpoints occurs on the theoretical part, of the same nature as with the higher alcohols, the result being that at low temperatures the cross-plait is cut through by one self-contained liquid-plait. But as far as the phenomena are concerned this is entirely immaterial.

As far as the experiments could be carried (i.e. up to 275 atmospheres) the critical curve continued to rise towards the left, so that there is no indication of the existence of a different plaitpoint. The rapidity with which the mixing-pressure increases is truly remarkable.

If we compare the figures for methylalcohol and for the higher terms, a certain resemblance will be noticed, especially if we do not assume the contraction of the closed plait to nothing in the latter case. The association tends to produce the same modification in the usual diagram in both cases, but the acting causes appear to be much more effective with methylalcohol — the stronger association of the alcohol, possibly a smaller mutual attraction or the influence suggested by Prof. VAN DER WAALS of the small molecular volume of the alcohol may contribute to this result. For this substance the plaitpoint remains outside the cross-plait at low temperatures, with the others it succeeds in disappearing inside. Whether inside this plait any changes take place similar to those occurring with methylalcohol on the practical part of the surface we cannot tell. But in any case I have assured myself that with ethylalcohol a new plaitpoint curve does not appear down to -78° : ethylalcohol and ethane remain miscible in all proportions.

Methylalcohol and ethane mix by pressure. In this respect they contrast with mixtures phenol and water for which the liquid plait above a certain temperature far below the critical region separates completely from the cross-plait and thus has a plaitpoint on the side of the positive τ -axis. In view of the probable disappearance of the association at high temperatures it is possible that in the latter case

¹⁾ Continuität etc. II. p. 191.

further experiments will disclose a second plaitpoint on the liquid side of the plait, as predicted many years ago by VAN DER WAALS from the value of the volume-constants. I expect to be able to throw more light on this subject by the continuation of my investigation with the higher hydrocarbons. Ether and water behave in all probability in a manner similar to methylalcohol and ethane.

Chemistry. — “*On the so-called compounds of salts of sulphon-carboxylic acids with sulphuric esters.*” By Prof. A. P. N. FRANCHIMONT.

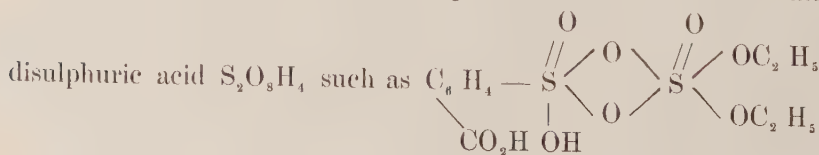
(Communicated in the meeting of January 31, 1903).

The first of this kind of compounds was obtained accidentally by LAUBE in 1879 in the laboratory of GEUTHER in Jena. He wanted to reduce sodium sulphonacetate with sodium amalgam and water, but after acidifying with sulphuric acid, evaporating, and extracting with absolute alcohol, he obtained an acid liquid which gave with barium carbonate a salt of the empirical composition $C_6H_{14}BaS_2O_{10}$. This salt has, therefore, the composition of one molecule of barium sulphonacetate plus one molecule of ethyl sulphate plus one molecule of water and may, according to GEUTHER, be considered as a derivative of a disulphuric acid in which two hydrogen atoms have been replaced by ethyl groups and one OH group by the group CH_2-COOH . He obtained the same compound by digesting a mixture of sodium sulphonacetate, sodium-hydrogen sulphate and alcohol. The acid was called “*Diäthylsulfidischwefelsäure*”. Acetic acid itself did not yield a similar compound.

In 1883, in the same laboratory, STENGEL successfully attempted to obtain a similar compound with metasulphobenzoic acid; the analysis gave the composition $C_{11}H_{14}O_7S_2Ba + 3\frac{1}{2}H_2O$. The acid was called “*Diäthylbenzoeschwefelsäure*”. Analogous compounds were also obtained with methyl and propyl alcohol. Benzoic acid, however, did not give a similar compound and it is, therefore, attributed to the sulphonic acid group.

ENGELCKE obtained similar compounds with isethionic acid but not with benzenesulphonic acid and NITACK did not obtain it with methylsulphonic acid.

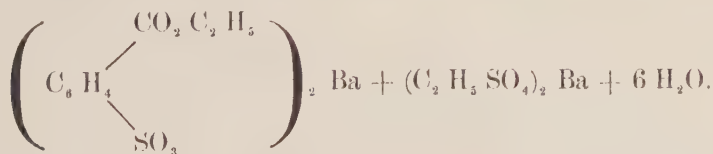
GEUTHER looked upon these compounds as salts of a derivative of



In BEILSTEIN'S "Handbuch", however, these compounds are described as double compounds of salts of sulphoncarboxylic acid with neutral sulphuric esters.

For a long time, however, I have felt serious objections to this theory. I had already repeated the experiments with sulphonacetic acid and metasulphobenzoic acid but did not obtain pure compounds. I was also unsuccessful in attempting a synthesis by means of the salts of sulphoncarboxylic acids and dimethyl- and diethylsulphate. The phenomena observed during this research induced me to request Dr. ATTEMA to try to obtain compounds of the same empirical composition in a different manner, namely by bringing together in molecular proportions the barium salts of the acid esters of metasulphobenzoic acid with the barium salts of the alkylsulphuric acids. If in this proportion they yield a compound this ought then to have the same empirical composition as the last named compound.

Dr. ATTEMA now observed that on evaporating a solution containing in molecular proportions the barium salt of the ethyl ester of metasulphobenzoic acid and barium ethylsulphate, the greater portion of the ethylbarium salt of metasulphobenzoic acid was deposited first in beautiful crystals; after this a double compound of the two barium salts made its appearance in the form of large rosettes of tender needle-shaped crystals whilst from the motherliquor barium ethylsulphate was obtained. If an excess of barium ethylsulphate is taken for instance, 5 grams of the same to 1 gram of the salt of barium ester the double compound separates immediately and from the motherliquor barium ethylsulphate is obtained. The double compound cannot be recrystallised from water; its aqueous solution presents the same phenomena as one containing in molecular proportion the two salts; on evaporation, the salt of barium ester crystallises first, then the double compound and finally the barium ethylsulphate. As the double compound cannot be recrystallised from alcohol it was freed from motherliquor by strong pressure and analysed. The results of the analyses of three different preparations were concordant and agreed with the formula:



Dr. ATTEMA has afterwards repeated STENGEL'S method of preparing the compounds, but here he also obtained first the ethyl barium salt of metasulphobenzoic acid and afterwards, although less readily,

the double compound. An analogous result was obtained with the methyl compound.

We may, therefore, come to the conclusion that there exist no compounds of salts of sulphoncarboxylic acids with neutral sulphuric esters; there exist, however, double compounds of salts of the acid esters of sulphoncarboxylic acids with salts of the acid sulphuric esters. This result gives rise to a number of questions some of which Dr. ATTEMA intends answering by practical experiments. Both salts are alkyl-metallic salts of dibasic acids whose acidic functions (at all events in the case of metasulphobenzoic acid) have a very different power, whilst sulphuric acid as oxysulphonic acid is somewhat comparable to isethionic acid which also exhibits the property.

Mathematics. — “*On the spheres of MONGE belonging to ordinary and tangential pencils of quadratic surfaces.*” By Prof. JAN DE VRIES.

1. In Part I of the “Proceedings of the Section of Sciences” pages 305—310, I have developed, making use of FIEDLER’s cyclographic representation, some properties with respect to the system of the orthoptical circles of the conics of a linear system. By extending FIEDLER’s considerations to a four-dimensional space the corresponding case of the three-dimensional space might be treated. In the following essay the indicated extension on quadratic surfaces is arrived at analytically.

Given P the point of intersection of three mutually perpendicular tangent planes of the quadratic surface S^2 represented by the equation

$$a_{11}x^2 + a_{22}y^2 + a_{33}z^2 + 2a_{12}xy + 2a_{13}xz + 2a_{23}yz + 2a_{14}x + 2a_{24}y + 2a_{34}z + a_{44} = 0.$$

These three tangent planes form with every fourth tangent plane a tetrahedron circumscribed about S^2 that may be regarded as polar tetrahedron with respect to the point-sphere (isotropic cone) I^2 represented by

$$(x-x_1)^2 + (y-y_1)^2 + (z-z_1)^2 = 0.$$

So the invariant Θ belonging to S^2 and I^2 is equal to zero¹⁾. Therefore we have:

¹⁾ See a.o. SALMON-FIEDLER, Anal. Geom. des Raumes, 3d edition, vol. I, p. 253, where S^2 is represented by an ellipsoid.

$$\begin{vmatrix} a_{11} & a_{12} & a_{13} & -x_1 \\ a_{12} & a_{22} & a_{23} & -y_1 \\ a_{13} & a_{23} & a_{33} & -z_1 \\ a_{14} & a_{24} & a_{34} & (x_1^2 + y_1^2 + z_1^2) \end{vmatrix} + \begin{vmatrix} a_{11} & a_{12} & 0 & a_{14} \\ a_{12} & a_{22} & 0 & a_{24} \\ a_{13} & a_{23} & 1 & a_{34} \\ a_{14} & a_{24} & -z_1 & a_{44} \end{vmatrix} + \\
+ \begin{vmatrix} a_{11} & 0 & a_{13} & a_{14} \\ a_{12} & 1 & a_{23} & a_{24} \\ a_{13} & 0 & a_{33} & a_{34} \\ a_{14} & -y_1 & a_{34} & a_{44} \end{vmatrix} + \begin{vmatrix} 1 & a_{12} & a_{13} & a_{14} \\ 0 & a_{22} & a_{23} & a_{24} \\ 0 & a_{23} & a_{33} & a_{34} \\ -x_1 & a_{24} & a_{34} & a_{44} \end{vmatrix} = 0.$$

If we represent the minor of a_{ik} in $\Delta = \sum \pm a_{11} a_{22} a_{33} a_{44}$ by A_{ik} , it ensues from this relation that the locus of the point P is indicated by the following equation (where the indices of the coordinates are left out)

$$A_{44}(x^2 + y^2 + z^2) - 2(A_{14}x + A_{24}y + A_{34}z) + (A_{11} + A_{22} + A_{33}) = 0.$$

So the locus of the points of intersection of triplets of mutually perpendicular tangent planes of S^2 is a sphere (MONGE).

The tangential cone to S^2 with vertex P possessing three mutually perpendicular tangent planes, the tangent planes form according to a well-known property an infinite number of triplets of mutually perpendicular planes.

For $A_{44} = 0$ we find S^2 to be a paraboloid and the sphere of MONGE degenerates into a plane.

The obtained equation can be replaced by

$$\left(x - \frac{A_{14}}{A_{44}}\right)^2 + \left(y - \frac{A_{24}}{A_{44}}\right)^2 + \left(z - \frac{A_{34}}{A_{44}}\right)^2 = \frac{1}{A_{44}^2} \sum (A_{14}^2 - A_{11}A_{44}).$$

Now however $A_{11}A_{44} - A_{14}^2$ is equal to $(a_{22}a_{33} - a_{23}^2) \Delta^{-1}$

The radius of the sphere is indicated by the square root out of

$$-\frac{\Delta}{A_{44}^2} \sum (a_{22}a_{33} - a_{23}^2).$$

Consequently the sphere of MONGE will be reduced to a point-sphere when S^2 is a cone ($\Delta=0$) or into an equilateral hyperboloid if namely the equation

1) This ensues inter alia from

$$\begin{vmatrix} a_{11} & a_{12} & a_{13} & a_{14} \\ a_{12} & a_{22} & a_{23} & a_{24} \\ a_{13} & a_{23} & a_{33} & a_{34} \\ a_{14} & a_{24} & a_{34} & a_{44} \end{vmatrix} \times \begin{vmatrix} A_{11} & A_{12} & A_{13} & A_{14} \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ A_{14} & A_{24} & A_{34} & A_{44} \end{vmatrix} = \begin{vmatrix} \Delta & a_{12} & a_{13} & 0 \\ 0 & a_{22} & a_{23} & 0 \\ 0 & a_{23} & a_{33} & 0 \\ 0 & a_{34} & a_{34} & \Delta \end{vmatrix}$$

(See a. o. BALTZER, Determinanten, 5th edition, p. 63).

$$(a_{11}a_{22} - a_{12}^2) + (a_{22}a_{33} - a_{23}^2) + (a_{33}a_{11} - a_{13}^2) = 0$$

is satisfied.

In the latter case the asymptotic cone possesses as is known ∞^1 triplets of mutually perpendicular tangent planes.

2. When in the equation

$$A_{11}(x^2 + y^2 + z^2) - 2(A_{11}x + A_{21}y + A_{31}z) + (A_{11} + A_{22} + A_{33}) = 0$$

we substitute $a_{ik} + \lambda b_{ik}$ for a_{ik} , the new equation represents the system of the spheres of MONGE belonging to the quadratic surfaces of a pencil.

The equation is a cubic one in λ ; so the indicated spheres form a system with index 3, that is, through each point three spheres pass.

If for brevity's sake we represent the formula

$$x^2 + y^2 + p_k x + q_k y + r_k$$

by C_k , the cubic equation is

$$l_0 C_0 \lambda^3 + l_1 C_1 \lambda^2 + l_2 C_2 \lambda + l_3 C_3 = 0.$$

The power of a point with respect to the sphere (λ) is then equal to

$$\frac{l_0 C_0 \lambda^3 + l_1 C_1 \lambda^2 + l_2 C_2 \lambda + l_3 C_3}{l_0 \lambda^3 + l_1 \lambda^2 + l_2 \lambda + l_3}.$$

This expression becomes independent of λ for the centre of the sphere cutting the four spheres C_k orthogonally; *all the spheres of the indicated system are intersected at right angles by a fixed sphere.*

On this *orthogonal sphere* the point-spheres of the system are of course situated; so it contains in the first place the *vertices* of the four *cones*, in the second place the *centres* of the two *equilateral hyperboloids*¹⁾ belonging to the pencil.

From this ensues that the locus of the centres of the spheres is a skew cubic. This is moreover confirmed by the observation that in

$$x_0 = A_{11} : A_{44}, \quad y_0 = A_{24} : A_{44}, \quad z_0 = A_{34} : A_{44}$$

the numerators and the denominators are cubic forms in λ .

The square of the radius being represented by the quotient of two forms of order six in λ , the system contains six spheres with given radius.

3. The quadratic surface indicated by the equation in tangential coordinates ξ, η, ζ

¹⁾ Their parameters are determined by

$$\sum_3 [(a_{11} + b_{11} \lambda)(a_{22} + b_{22} \lambda) - (a_{12} + b_{12} \lambda)^2] = 0.$$

$$\sum_3 a_{11} \xi^2 + 2 \sum_3 a_{12} \xi \eta + 2 \sum_3 a_{13} \xi + a_{14} = 0$$

has for equation in point coordinates

$$\sum_3 A_{11} x^2 + 2 \sum_3 A_{12} x y + 2 \sum_3 A_{14} x + A_{44} = 0.$$

If now a_{ik} is the minor of the determinant $\sum \pm A_{11} A_{22} A_{33} A_{44}$ corresponding to A_{ik} , the sphere of MONGE of the indicated surface is represented by

$$a_{11}(x^2 + y^2 + z^2) - 2(a_{11}x + a_{21}y + a_{31}z) + (a_{11} + a_{22} + a_{33}) = 0.$$

But we have ¹⁾ $a_{ik} = a_{ik} \mathcal{L}^2$; so this equation can be replaced by

$$a_{44}(x^2 + y^2 + z^2) - 2(a_{14}x + a_{24}y + a_{34}z) + (a_{11} + a_{22} + a_{33}) = 0,$$

or by

$$\left(x - \frac{a_{14}}{a_{44}}\right)^2 + \left(y - \frac{a_{24}}{a_{44}}\right)^2 + \left(z - \frac{a_{34}}{a_{44}}\right)^2 = \frac{1}{a_{44}^2} \sum_3 (a_{24}^2 - a_{11} a_{44}).$$

So for a tangential pencil of quadratic surfaces we find

$$(a_{44} + b_{44} \lambda)(x^2 + y^2 + z^2) - 2 \sum_3 (a_{14} + b_{14} \lambda)x + \sum_3 (a_{11} + b_{11} \lambda) = 0,$$

that is, the corresponding spheres of MONGE form a pencil.

To this belong the point-spheres indicated by

$$\sum_3 [(a_{14} + b_{14} \lambda)^2 - (a_{11} + b_{11} \lambda)(a_{44} + b_{44} \lambda)] = 0,$$

originating from two equilateral hyperboloids, and the plane determined by $a_{44} + b_{44} \lambda = 0$ belonging to the paraboloid of the tangential pencil.

Physics. — “*The variability with the density of the quantity b of the equation of state.*” By Dr. J. D. VAN DER WAALES JR. Communicated by Prof. J. D. VAN DER WAALES.

§ 1. If we suppose the molecules of a gas ²⁾ to be perfectly smooth, elastic spheres, the influence of the fact that their diameter is not infinitely small, on the form of the equation of state may be allowed for in first approximation by diminishing the volume V , in which the gas is contained, with four times the volume of the molecules. If we understand by distance sphere a sphere described concentric with a molecule and with a radius 2σ (where σ denotes the

¹⁾ See inter alia BALTZER, l. c. p. 65.

²⁾ I say only “gas” not “gas or liquid”, for we must not apply the formula for a liquid without introducing still other approximated terms than those that will be discussed here.

radius of the molecule), then we may also say, that we must diminish V with half the combined volumes of the distance spheres, which quantity is usually denoted by b , or by b_{∞} if we wish to take into account the variability of the correction in consequence of variation in density. Various methods have been followed in order to investigate this influence; all these methods yielded a conformable result, so that no reasonable doubt can exist as to the correctness of this statement.

We should be inclined to deduce from this, that the influence may be correctly allowed for in second approximation by diminishing V with half the volume really occupied by the distance spheres, in which a segment which two distance spheres have in common, is counted only once, or what comes to the same, by writing $b_{\infty} - \Sigma S$ instead of b_{∞} , ΣS representing the sum of all the segments which are covered by two distance spheres at the same time. The correction has been introduced in this way by Prof. J. D. VAN DER WAALS ¹⁾; and Dr. J. J. VAN LAAR ²⁾ has made a calculation of a second correction term, which is based on a similar supposition. I will however confine myself to the discussion of the first correction term, for which we find in this way $\frac{17 b_{\infty}^2}{32 V}$. The question whether the first correction

term is correctly found in this way has not been answered unanimously in the affirmative. BOLTZMANN ³⁾ follows quite a different

method for calculating it and finds $\frac{3 b_{\infty}^2}{8 V}$. Though BOLTZMANN in his

communication in these Proceedings expressed the wish that his publication of this result differing from my father's would give rise to a discussion by which this doubtful point might be elucidated, no discussion has followed by which the question has been settled conclusively. Now I think I can show that there is no reason for

introducing the correction in the way which yields the value $\frac{17 b_{\infty}^2}{32 V}$,

and at the same time I will give a reasoning, by which the term $\frac{3 b_{\infty}^2}{8 V}$ is derived in a shorter way than that followed by BOLTZMANN.

The simplest way to show clearly what supposition we must make in order to get the correction term $\frac{17 b_{\infty}^2}{32 V}$ is to start from the

¹⁾ Versl. Kon. Akad. v. Wetensch. V. p. 150. Oct. 1896.

²⁾ These Proceedings Vol. I, p. 273. Jan. 1899.

³⁾ These Proceedings Vol. I, p. 398. March 1899; and "Vorlesungen über Gastheorie" II, p. 151.

virial equation as my father has done for the external pressure and for the pressure of the molecular attraction in Chapter II of his "De Continuïteit van den Gas- en Vloeïstoofstand" and for the forces eventuating in collisions of two molecules in these Proceedings Vol. I, p. 138. Oct. 1898.

First, however, I will point out, that the virial equation need not necessarily be applied for a definite quantity of matter, which is contained in a definite volume and enclosed within a solid wall, as is the usual method of applying it. We may as well apply that equation for a part of a homogeneous phase, separated by an imaginary separating surface from the surrounding substance which is in the same phase. We shall not always find *the same* molecules within such a surface, but we may assume, that at two different instants t_1 and t_2 we shall find *the same number* or at least with very great approximation the same number of molecules within it, and that the expression $\sum m v \frac{dx}{dt}$ will also have the same value at the instants t_1 and t_2 . We may therefore put:

$$\frac{d}{dt} \sum m v \frac{dx}{dt} = 0$$

and also the corresponding equations for the y - and for the z -coordinate.

From this we may deduce:

$$\sum m s^2 = - \sum \left[x \frac{d m \dot{x}}{dt} + y \frac{d m \dot{y}}{dt} + z \frac{d m \dot{z}}{dt} \right] \dots \dots (A)$$

In the case that we may neglect the volume of the molecules with regard to the volume in which they are contained, and that we may assume that the molecular forces act in such a way that they yield on average zero for the force exercised on a molecule within a homogeneous phase, the righthand member of this equation has only a value at the border of the volume under consideration; it may therefore be reduced to a surface-integral.

The lefthand member of this equation is independent of the circumstance whether the space under consideration is enclosed within an imaginary separating surface or within a solid wall, and in the latter case it is also quite independent of the properties of this wall. So the righthand member cannot depend upon these circumstances either. In the case of a solid wall we may write: $\frac{dm}{dt} = 0$. So we get for the righthand member:

$$-\int P' r \cos (n, r) d\sigma = 3 P' V \quad . \quad . \quad . \quad . \quad . \quad (B)$$

Here r represents the radius vector drawn from the origin of the system of coordinates to a point of the surface, $d\sigma$ represents an element of that surface, $\cos (n, r)$ the cosine of the angle which the radius vector forms with the normal to the surface. P' is the force per unit of surface which prevents the molecules to leave the space and compels them to return towards the inside of it. We may distinguish in it the molecular pressure $\frac{a}{v^2}$ and the pressure p exercised by the wall.

For the case of an imaginary separating surface, $\frac{d}{dt} m \frac{dx}{dt}$ is the momentum in the direction of the positive x -axis conveyed through the surface to the inside of it. Momentum conveyed to the outside has to be taken into account with the negative sign. In this case also the righthand member may be represented by equation (B) though here the symbol P' does not any longer represent a force which really acts on the molecules.

In the case that the volume really occupied by the molecules is not so small that we may neglect it, also the virial of the forces eventuating in the mutual collisions of the molecules must be taken into account. If we denote this virial by I then we may write equation (A)* in the following form:

$$\Sigma ms^2 = -I - \int P r \cos (n, r) d\sigma = -I + 3 PV.$$

Σms^2 and I being independent of the properties of the bordering surface, P cannot depend upon them either. P appears to be greater than P' ; for a wall this is because the number of collisions is augmented in consequence of the abbreviation of the mean length of path which a molecule describes between two successive collisions; for an imaginary separating surface this is because the conveyance of momentum through that surface has augmented in consequence of the fact that in collisions between two molecules whose centers lie at opposite sides of the separating surface, the momentum is transplacated instantaneously from the center of one molecule to that of the other; so the momentum has been transported with infinite velocity.

But the way in which we have derived the quantity P which may be estimated to represent the pressure prevailing in the gaseous or in the liquid phase, warrants in any case that this quantity is

independent of the shape of the vessel and the properties of the walls in which the phase is enclosed, but on the other hand it warrants also that we may find the quantity P by calculating the pressure which would be exercised against a plane wall if the molecules did not attract one another, or by adding $\frac{u}{v^2}$ to the pressure exercised by mutually attracting molecules against a plane wall.

The way in which the virial of the forces eventuating in mutual collisions of the molecules has been introduced by Prof. VAN DER WAALS is as follows. We assume that in first approximation P represents also the pressure exercised on the distance spheres of the molecules. This would yield the value $2 Pb_{\infty}$ for the virial. We must, however, take only half this value, else all the forces would have been counted twice.

The distance spheres, however, cannot be considered as unmoving solid walls, but as moving and movable walls and therefore it is perhaps not quite superfluous to show expressly that they are indeed subjected to a pressure amounting in first approximation on average to P . I will give the proof of this proposition in § 2 of this communication.

The introduction of the correction term $\frac{17}{32} \frac{b^2}{V}$ is based on the consideration that the value of the virial given above will be too great because some of the distance spheres partly coincide. The parts of the surface of a distance sphere I falling within a distance sphere II are protected from collisions with all other molecules but II. Therefore the pressure on such parts is assumed to be zero; on the other parts the pressure on the distance spheres is supposed to be P . This comes to the same as the assumption that the average pressure during a time τ (and every pressure which we consider, the pressure P also, cannot be anything else but an average value during a certain time τ) exercised on an element $d\sigma$ of a distance sphere would be smaller than P , because of the fact that the element $d\sigma$ is only during a part of the time τ exposed to the pressure P , during another part of that time, however, it would have been subjected to no pressure, because it was protected by the distance sphere of a molecule II from collisions with other molecules.

I have two objections to the calculations based on these considerations.

In the first place the assumption is made, that a part of a distance sphere would never experience any pressure, when it lies within the distance sphere of another molecule. In fact the reverse is true: in order that a surface element should experience a pressure, a

molecule must collide against it and then it lies in the distance sphere of that molecule; and the considerations in which the pressure inside the distance spheres is assumed to be zero, outside them to be P , are certainly not a correct representation of what really happens. Yet points lying inside distance spheres are in somewhat different conditions as to the pressure that may be exercised on them, than points outside distance spheres. It is not clear to me how these conditions should be taken into account. It is, however, not necessary to know this in order to calculate the correction term, as will appear from my second objection.

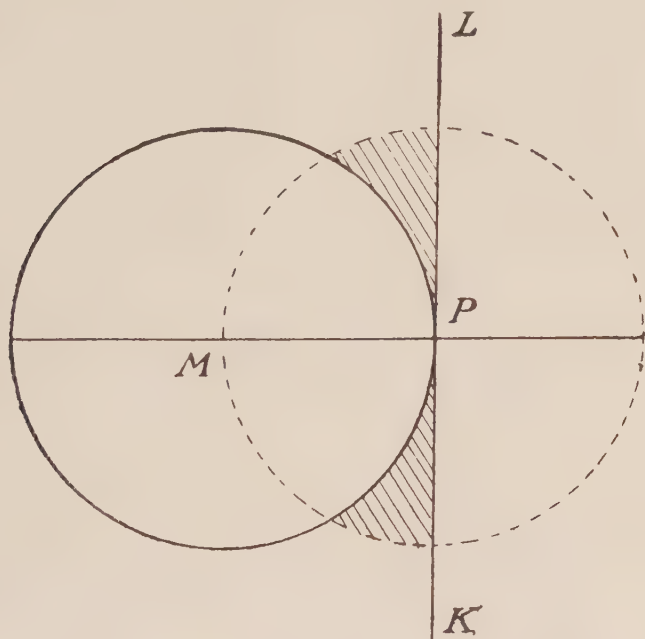
In the second place the fact has been overlooked that not only some parts of distance spheres lie within other distance spheres but that the same circumstance occurs for parts of the bordering surface. It is indifferent whether this is an imaginary surface or a solid wall ¹⁾, in any case a part of it will lie within the distance spheres of the molecules, and may therefore with as much (or as little) right be estimated to be protected from pressure. Now let $1/\lambda$ part of the bordering surface lie within the distance spheres. If we must assume that this part of the surface experiences a pressure zero, and that the free surface experiences a certain pressure, that we will call P_1 , then the quantity P , which represents — as appears from the way in which it has been introduced — the average pressure, would be equal to $\frac{\lambda-1}{\lambda} P_1$. Let us now investigate what part of the total surface of the distance spheres lies within other distance spheres, and let $1/\lambda_1$ represent that fraction, then the average pressure of a distance sphere will amount to $\frac{\lambda_1-1}{\lambda_1} P_1$. If λ_1 were equal to λ , then the average pressure on the bordering surface and on the distance spheres would be the same, and we should not have to apply any correction to the term b_∞ .

We find the correction term $\frac{17b^2}{32V}$ if we make the following assumption, but only in that case: every surface element, — no matter whether it is a part of a solid wall or of an imaginary separating surface, and whether the surface is plane or curved and no matter whether it lies within or without the distance spheres of molecules —

¹⁾ The virial of the forces exercised by the wall must properly not be integrated over the wall itself, but over the surface which contains the centers of the molecules colliding against the wall, i. e. over a surface parallel to the wall and lying at a distance σ from it.

it will always experience a pressure P . Only the distance spheres make an exception to this rule, for parts of them, falling within other distance spheres experience a pressure zero.

I can find no reason for this exception and therefore I think the value $\frac{17}{32} \frac{b^2}{V}$ incorrect. The question whether in fact a correction must be applied depends on the fact whether λ_1 is equal to λ or not. This may be investigated in the following manner.



Let M in the figure represent the center of a molecule and let the circle described with M as center, represent the section of the distance sphere (I) of that molecule with the paper. Now we are to calculate the average pressure exercised during a time τ on a surface element do , the center of which we call the point P . To this purpose we describe a circle II with P as center and with a radius 2σ and we also consider the tangent plane in P which we call LK .

Two cases may be distinguished:

1st The space within sphere II but outside sphere I and at the left of the tangent plane (the section of the space in question with the paper has been hatched in the figure) may contain the center of a molecule; if this is the case P lies within the distance sphere of that molecule.

2nd The space under consideration may not contain the center of any molecule.

We will call that part of the time τ during which the former takes place $\frac{\tau}{\mu}$; so that part during which the latter takes place

$\frac{\mu-1}{\mu}\tau$. During the time $\frac{\mu-1}{\mu}\tau$ the surface element do is quite in

the same circumstances as an element of a plane wall. Therefore it will experience on average a pressure P . This pressure P is a quantity which we may derive from the virial equation; in order to determine it, it is therefore not required to decide whether the considerations

in consequence of which we find P equal to $\frac{2-1}{2}P_1$ are correct or

not. But when the former case takes place, so during the time $\frac{\tau}{\mu}$,

we are certainly justified in assuming that do does not experience any pressure. The average pressure on do is therefore $\frac{\mu-1}{\mu}P$.

We may find the value of μ in first approximation by determining the volume v of the hatched space, and by assuming that the chance that a certain definite molecule will lie within that volume is equal to $\frac{v}{V}$. If n denotes the total number of molecules, then the chance

that the space contains a molecule will be represented by $n\frac{v}{V}$. On average the value of $1/\mu$ will be equal to this chance; therefore in first approximation $1/\mu = n\frac{v}{V}$.

We find by a simple calculation for v the value $\frac{1}{4}\pi r^3$, where $r = 2\sigma =$ the radius of a distance sphere. Therefore:

$$1/\mu = n\frac{\frac{1}{4}\pi r^3}{V} = \frac{3}{8}\frac{b_\infty}{V}.$$

The internal virial I will therefore be $3Pb_\infty\left(1 - \frac{3}{8}\frac{b_\infty}{V}\right)$ and equation (A) assumes the following shape:

$$\frac{1}{3}\sum m s^2 = PV - Pb_\infty\left(1 - \frac{3}{8}\frac{b_\infty}{V}\right) = P\left(V - b_\infty + \frac{3}{8}\frac{b_\infty^2}{V}\right).$$

§ 2. In order to introduce the internal virial I I started from the supposition that the distance spheres of the molecules experience a pressure which is on average equal to P . As I never found a direct proof of this thesis I will give it here. The pressure P namely may i. a. be considered to represent the pressure exercised against a solid unmovng wall, disregarding the molecular pressure. The distance spheres, however, are not to be regarded as a solid, unmovng wall. In consequence of their motion the number of collisions against a surface element do of a distance sphere is greater than that on an equal element of the wall; moreover the force in each collision is proportional to the relative velocity of the molecules, which is greater than the velocity of each molecule separately.

From these two circumstances we are apt to assume that the average pressure on the distance spheres would be greater than P .

On the other hand the impulse of a molecule colliding with a velocity s normally against a solid, unmovng wall is $2ms$. If, however, the molecule collides with the velocity s centrally against another unmovng molecule with the same mass, then the first molecule will be stopped and the second will obtain the velocity s ; so the impulse is in this case only ms .

In consequence of this circumstance we should be inclined to expect the pressure on a distance sphere to be smaller than P .

The following simple calculation will suffice to show that these influences cancel each other and that the pressure exercised on the distance spheres is really equal to P , at least in the case that we may neglect the volume of the molecules with regard to the volume in which they are contained.

Let us imagine two molecules I and II with the same mass. The same proposition might be proved without difficulty also for mixtures, so for molecules with unequal masses, but I will confine myself here to molecules with the same mass. The velocities of the molecules will be denoted by s and s_1 and the components of these velocities by u, v, w and u_1, v_1, w_1 . The chance that molecules occur whose velocities have these components will be represented by $F(u, v, w)$ and $F(u_1, v_1, w_1)$ and the relative velocity by s_r . Then we have:

$$s_r^2 = (u - u_1)^2 + (v - v_1)^2 + (w - w_1)^2.$$

If we take the direction of s_r as the axis of a system of spherical coordinates, and if we call the latitude φ the longitude ψ , then a surface element of the distance sphere of molecule I will be represented by $r^2 \sin \varphi d\varphi d\psi$. The number of collisions per unit of time of molecules of group II against such a surface element is:

$$F(u, v, w) F(u_1, v_1, w_1) du dv dw du_1 dv_1 dw_1 s_r^2 \sin \varphi \cos \varphi d\varphi d\psi.$$

Not the total relative velocity s_r changes its sign in a collision of this kind, but only the component normal to the tangent plane in the point in which the molecules touch one another. The impulse is therefore $m s_r \cos \varphi$.

The total impulse of the collisions of the kind under consideration will therefore be equal to:

$$F(u, v, w) F(u_1, v_1, w_1) du dv dw du_1 dv_1 dw_1 s_r^2 r^2 \sin \varphi \cos^2 \varphi d\varphi d\psi.$$

The eightfold integral of this expression yields the total pressure exercised on the surface of the distance spheres. We have:

$$\iint r^2 \sin \varphi \cos^2 \varphi d\varphi d\psi = \frac{2}{3} \pi r^2$$

if we integrate according to ψ between the limits 0 and 2π and according to φ between the limits 0 and $\frac{1}{2}\pi$. The limits for φ are not 0 and π , for the parts of the distance sphere of molecule I for which $\varphi > \frac{1}{2}\pi$, cannot come into collision for the given relative velocity s_r . We may write $s^2 + s_1^2$, for s_r^2 for the terms $ss_1 \cos(s, s_1)$ yield zero on average. Doing this we may integrate the term with s^2 according to du_1 , dv_1 and dw_1 ; so we get:

$$\int F(u_1, v_1, w_1) du_1 dv_1 dw_1 = n.$$

The term with s_1^2 on the other hand may be integrated according to du , dv and dw ; so we get:

$$\int F(u, v, w) du dv dw = n.$$

This yields for the total pressure on the surface of the distance spheres:

$$\frac{2}{3} \pi r^2 n \left[\int m s^2 F(u, v, w) du dv dw + \int m s_1^2 F(u_1, v_1, w_1) du_1 dv_1 dw_1 \right].$$

Both integrals in this expression are equal to $n m s^2$, $m s^2$ representing twice the mean kinetic energy of a molecule. We may therefore write this expression as follows:

$$\frac{4}{3} \pi r^2 n^2 m s^2.$$

Dividing this quantity by the total surface of the distance spheres $4\pi r^2 n$, we get for the value of the average pressure:

$$\frac{1}{3} n m s^2.$$

This is the same value as we find for the pressure exercised on a solid, unmoving wall.

In order to calculate the number of collisions we have here neglected the extension of the molecule and the mutual attraction of the molecules. Therefore it is apparent that we cannot have obtained anything else but a first approximation.

Botanics. — “*Die Stelin-Theorie*”, Dissertation of Mr. J. C. SCHOUTE.
(Communication of Prof. J. W. MOLL).

According to the idea of VAN TIEGHEM, given about the tissues of root and stem of the vascular plants, they must be divided into three groups or systems of tissues, namely, epidermis, cortex and central-cylinder. It is such a natural thing to call the epidermis a separate tissue that already a long time before VAN TIEGHEM, it was acknowledged and is at present generally accepted.

It is a different thing about the theory that the central part of stem and root is taken up by a cylinder of tissue, the central-cylinder (or “*stèle*”), which may consist of elements differing greatly, but which must nevertheless be regarded as a connected whole, forming a certain contrast with respect to the cortex. This consideration which can be called the “*Stelar-theory*” is accepted by some, rejected by others. It is of the greatest importance for instruction and for the construction of descriptions of the inner structure, and it has undoubtedly for both these reasons such a great practical weight, that for this reason only it deserves our attention in a high degree. The scientific foundations for this theory are not in such a good condition and assuredly its non-acceptance is owing to this. Of course the important question is, whether this distinction between cortex and central-cylinder has made its appearance already at an early period in the phylogeny of plants. With the present state of our knowledge this can perhaps not be proved with certainty; but to be able to answer this question in the affirmative two conditions must be put: 1st. the central-cylinder must be indicated if not in all, still in the greater part of stems and roots, 2nd. it must appear already at an early period in the development of these organs.

As for the root these conditions are amply satisfied, which gives great support to the theory of VAN TIEGHEM. But this is not the case to such an extent for the stem, partly perhaps in connection with the complications formed already at an early period by the develop-

ment of the leaves, partly in connection with the splitting up of the central-cylinder in these organs of many plants. Concerning the latter point VAN TIEGHEM himself and of late a number of American and English investigators: GWYNNE-VAUGHAN, JEFFREY, BOODLE, FAUL, WORSDELL, BRETELAND FARMER & HILL, Miss FARD, TANSLEY & LULHAM, BREBNER have shed much light. In all those cases in which stems show a number of loose strings, regarded by some as parts of a central-cylinder (schizostely), by others as vascular bundles, a single central-cylinder, the monostelic structure, is rule in the youngest internodes of the plant, in hypo- and epicotyl and in the internodes following immediately.

But in most cases there is no question about schizostely and so according to VAN TIEGHEM we must expect monostely. However it is a fact, that whilst in every root the most superficial microscopic investigation easily proves the existence of a central-cylinder, this is not at all the case for many stems. The inner layer of the cortex (endodermis), it is true, is often developed as a bundle-sheath indicating as that of the root does, the boundary of the central-cylinder, or also it contains starch-grains, so that a distinct starch-sheath is formed; but in a great many other cases, also in an investigation made for that purpose, as was done by H. FISCHER, it has not been possible to point out a well defined central-cylinder. FISCHER found in 100 investigated plants only in 32 cases a distinct endodermis.

It has now been shown by Mr. SCHOUTE that this objection to the Stelar-theory does not exist in reality. He collected out of the literature on this subject numbers of cases, in which a distinct endodermis had been observed in some shape or other. He himself studied a great number of stems of different plants and then it was evident how necessary it is to examine these organs in different and especially in young stages of their development, a thing FISCHER had not done. The result of this method of working was, that of about 400 dicotyledonous plants only in 7 no distinct endodermis was come across and among these 7 there were yet 4 which even showed a sharp boundary of the central-cylinder. Also the greater part of the Monocotyledonous plants possess an endodermis. It is not to be found in Gymnosperms but yet here as is the case in most of the above-mentioned exceptions, a distinct boundary between cortex and central-cylinder is often to be seen. So this result is very favourable for the Stelar-theory and is a contribution to its scientific confirmation.

But in yet another manner has Mr. SCHOUTE endeavoured to test the Stelar-theory, a test, which it is true has led to a negative result, but which enables us to draw weighty conclusions with regard to

the value of the well known Theory of the histogens of HANSTEIN.

In working out his theory VAN TIEGHEM purposely avoided as much as possible to make use of the history of development, and as has been proved justly. Yet it was quite natural to think that there was a connection between the structure of the full-grown stem and root and that of the same organs at a very early period of development, in embryo or growing point. For HANSTEIN had established a doctrine about the structure of the meristems, very much like VAN TIEGHEM's theory and had gained a number of adherents. He thought, especially on account of the arrangement of the otherwise equivalent cells, to be able to distinguish three tissues in those meristems, called dermatogen, periblem and plerome. The last was a column of cells in the middle part of the stem and root. Of course it was quite natural to think of an identity of dermatogen and epidermis, periblem and cortex, plerome and central-cylinder, in such a manner that the latter had developed out of the former. If it were possible to point out such a correspondence, this would be for the Stelar-theory as well as for the Theory of the histogens of great importance, though not of equal importance for both. If the central-cylinder is already found in the meristem as an independent whole, this points to the fact, that the differentiation of this tissue is old and then the Stelar-theory has gained another support. But as I said above, it is fully established in another way and can very well do without this support.

The HANSTEIN-theory of the histogens is a different case. Every one who studies the literature impartially, will have to own that this doctrine rests on a very weak foundation, perhaps not with respect to the dermatogen, but very certainly as far as the plerome is concerned. It is true, there are some roots and a very few stems in whose thin tops the cells are arranged in a remarkably regular order, so that a central-cylinder can be distinguished as plerome. But in many roots and in nearly all stems there is no question about tracing such an arrangement up to the growing-point. It is really to be wondered at that this HANSTEIN-theory in its generality has found so many genuine adherents; this is certainly partly owing to the conviction, expressed by many and silently shared by others, that plerome and central-cylinder are one and the same.

Yet this had never been accurately examined till it was undertaken by Mr. SCHOTTE. But it is clear, that a positive result would be of the greatest importance for this theory. For there is no sense in accepting histogens without full-grown tissues corresponding to them. Moreover might be expected of a positive result the possibility of finding an undoubted plerome when following the boundary of

the central-cylinder upwards, also in those cases in which up till now the efforts had not been successful, perhaps on account of the great number of cells.

The investigation of Mr. SCHOUTE was an accurate comparative study of connected series of cross and lengthwise sections. It would lead me too far if I were to speak of this more in particulars. But in general the investigation was conducted in such a way that an attempt was made to pursue in the direction of the growing point the boundary between the series of cells which could be distinguished as endodermis and central-cylinder in the older parts. The results were in short as follows.

Of the root of *Hyacinthus orientalis* and *Linum usitatissimum* the series of cells of the endodermis and the outer layer of the central-cylinder (pericycle) were successfully and uninterruptedly pursued up to the growing-point. In these cases a cylinder of tissue could be distinguished in the top, which could quite naturally be compared to the plerome of HANSTEIN and which corresponded exactly to the later central-cylinder. Also in *Helianthus annuus* in the main the same was found, though the plerome did not appear here as a complex of cells closed at the top. In the stem of *Hippurus vulgaris*, one of the few stems in which different investigators have distinguished a plerome, this was not only successfully found back, but also the series of cells of endodermis and pericycle could be pursued uninterruptedly to the growing-point. However the cells of the plerome proved to form not only the central-cylinder but also the endodermis and two layers of cells of the cortex, so that the required correspondence did not exist here. In the stem of *Elodea canadensis* an uncertain result was obtained, as here a starch-sheath and a bundle-sheath were found, and it was not possible to make out which of the two must be regarded as endodermis. But in the root of *Ficaria ranunculoides* and in the stalks of *Aesculus Hippocastanum*, *Lysimachia Ephemerum*, *Eronynus europaeus* and *Ajuga reptans* an important negative result was obtained. Here it was perfectly evident that the series of cells of endodermis and pericycle cannot be pursued up to the top, but that they very soon stop short and are replaced by shorter series of cells not exactly in their prolongation and which in their turn soon undergo the same fate. In other words in all these cases the expectation was not only disappointed that in this way in difficult cases a plerome was to be found, but it was also irrefutably established that it does not exist here.

After the above-mentioned explanations it need not be demonstrated that these results as a whole must be regarded as fatal to the Theory

of the histogens. That in some selected roots there is some correspondence, makes no difference. That in slender tops built up out of relatively few, lengthwise series of cells a regular arrangement of cells may appear as was described above, is the most natural thing in the world. To give a particular explanation of this is unnecessary, and in no case are these single indications sufficient to establish solely on them a theory of histogens as that of HANSTEIN. And yet this would have to be done if one wished to adhere to this theory, for all other facts plead strongly against it. *Hippuris*, almost the only plant showing a plerome in the stem, has a structure altogether opposed to the theory. And the irregularly built tops form without doubt the overpowering majority.

It seems to me that by the investigation of Mr. SCHOUTE the Histogen theory of HANSTEIN is proved to be erroneous. A conclusion of somewhat general importance can still be deduced from these investigations. Many botanists think that to the celldivision in meristems a certain phylogenetic importance must be given, somewhat comparable to that of the germinal layers in zoology. But here is forgotten that in zoology in the history of development folds and again folds are spoken of, to a certain extent also histological differentiation is mentioned, but little or nothing of directions of cell-division or of arrangements of otherwise entirely equivalent cells. If the zoologist attains at beautiful results by the study of the history of development, it in nowise ensues from this that the study of the arrangement of cells in meristems will be able to furnish these. Rather will the botanist have to expect such explanations from the study of the development of outer forms, and of inner differentiations as a result of differences in the nature of cells. Experience has taught us that this expectation has a right to exist. But the Histogen-theory has certainly contributed to nourish the above mentioned wrong opinion. Now that this has been proved to be incorrect we may expect that the historic and phylogenetic importance which has often been ascribed to the divisions and arrangements of nondifferentiated and perfectly equivalent meristemcells will be reduced to its right and very slight proportion.

Groningen, Jan. 29, 1903.

Physics. — “*Methods and apparatus used in the cryogenic laboratory. III. Baths of very uniform and constant low temperatures in the cryostat.*” Communication N°. 83 from the physical laboratory at Leiden by Prof. H. KAMERLINGH ONNES.

(Communicated in the meeting of December 27, 1902.)

§ 1. By means of the cryostat described in § 8, Comm. 14. Dec. '94, and § 3, Comm. 51. Sept. '99 we can obtain a bath of liquefied gas which is shut off from the atmosphere and boils at ordinary or diminished pressure. In such a bath the temperature is sufficiently uniform and constant for many experiments and measurements. If we use almost pure gases and if the evaporated gas is regularly recondensed by means of a compression apparatus, which as described in Comms. 14. Dec. '94, 53. Sept. '99 and 54. Jan. '00, does not contaminate the gas, the bath may be maintained as long as we wish. The operations in the bath itself as well as the addition of the liquefied gas can be watched through the observing glasses. Vacuum glasses are not required so that similar cryostats may be constructed for measuring apparatus of any dimensions. Before long we shall describe a cryostat where the gas apparatus and the bath are more independent.

I was led to describe the form of the cryostat, as it occurs in Comm. 51, through the communication of the results for the dielectric constants of liquid gases. (Comm. 52 Oct. '99), for which measurements only the temperatures of -90°C. or -182°C. were required. For other measurements, however, a measuring apparatus, once immersed in the cryostat, has been used at the whole range of temperatures between, -23°C. (boiling point of methyl chloride at ordinary pressure) and -210°C. (nitrogen at reduced pressure), given by methylchloride nitrous-oxide, ethylene, methane, oxygen and nitrogen as they were successively admitted into the cryostat.

For a long time improvements have been made in this cryostat by means of which we can attain a much greater uniformity and constancy in the temperature, while retaining the afore-mentioned advantages. A description of these alterations has now become necessary in order to judge of the accuracy of the temperature readings in the results from various measurements where we have availed ourselves of these improvements. These measurements will be treated in the next communications. Among others I mention here those bearing upon the isothermals of diatomic gases (Comms. 69 March '01

and 78, March '02) and the comparison between the platinum resistance thermometer and the hydrogen thermometer (Comm. 77 Febr. '02) In this description, as in Comm. 51. Sept. '99, it seems to me desirable to illustrate the use of the cryostat by means of a special example. We will consider the comparison of the hydrogen thermometer with the resistance thermometer where also a thermo-element had been immersed in the bath.

Plate I shows the cryostat and some of the auxiliary apparatus to scale, the connections are represented schematically. It has been drawn on a smaller scale than plate I of Comm. 51 Sept. '99, (which should be consulted together with the one now given) but it will suffice to give a survey of the whole arrangement and to show some of the alterations. While the details of the unmodified parts can be studied on plate I of Comm. 51, plate II of the present Communication shows the details of the parts enclosed by the dot-dash-line of plate I, as far as they are required for consideration of the new arrangements. The connection of the apparatus shown in Pl. I with the gas circulation can be seen in Pl. IV Comm. 51. The comparison of the platinum thermometer p and the hydrogen thermometer T_h and their connections to the other pieces of the apparatus are given in Comm. 77 Febr. '02 § 3. For the comparison of the thermo-element Θ I am as yet obliged to refer to the very rough diagram of 1896 (Pl. I of Comm. 27 Mai and June '96). The communication, however, of some results for which the temperatures have been determined by means of a thermo-element will soon call for a description of the recent considerable improvements in the use of the thermo-elements.

On plates I and II a correction thermometer ξ , which is entirely independent of the cryostat, will be seen besides the three measuring apparatus mentioned above. It serves in our case to indicate the mean temperature of the capillary of the hydrogen thermometer, or in general, the mean temperature of similar pieces of measuring apparatus occupying the same part of the cryostat. For this purpose two spirals of platinum wire are wound round a glass rod, the one for that part of the rod, where the temperature varies slowly ξ_2 , the other for that part where the temperature varies rapidly ξ_1 . By means of the leads ξ_{00} , connected to the places of contact ξ_{11} , ξ_{12} and ξ_{21} and emerging through the tube ξ_{01} , we can determine the resistance of these spirals.

§ 2. First we shall mention some small changes in the cryostat of Comm. 51 which have no relation to the question of keeping the temperature constant and uniform.

The jet of liquefied gas let in at a (plate I) is directed, by means of the cock h_6 and the filter f , against a glass wall from which it streams along the delivery spout D_1 into the bath, here a double beaker $B_{01} B_{02}$ (Pls. I and II), placed in the beakers B_1, B_2, B_3 of Pl. I Comm. 51. The cock and filter form part of a cover which as described in Comm. 51, may be removed together with S_1 and S_3 from the cryostat and may also be replaced by a syphon or a capillary with a cock outside the cryostat. The spreading of the jet over the wall may be watched through the windows V_1 , and the height of the liquid in the bath through the windows V_2 . The filter f serves principally to prevent opaque dust from the lead (oxide of copper etc.) from depositing just at the place where the jet touches the glass. In many cases, however, it happened in spite of the care taken in purification, that the liquefied gas itself, while evaporating under reduced pressure in the cryostat, had deposited a substance, formerly dissolved in it but solid at the lower temperature, thus rendering the bath opaque. Therefore, differing from Comm. 51, a glass beaker C_1 (Pls. I and II) with numerous openings in the bottom C_{10} (Pl. II) and containing some glass wool was suspended by the regenerator spiral b (Pl. I Comm. 51). This filter may be lifted from the cryostat together with the piece S_6 .

With the arrangement as described in Comm. 51 all the gas, formed after the liquid leaves the cock, goes in the direction indicated by the arrows on Pl. I Comm. 51. With the arrangement as described here, however, the gas which is formed while the bath is being filled follows in the main a different direction to that which afterwards evaporates from the bath. In fact, differing from Comm. 51, a valve D_{110} with a spring D_{12} has been added, which almost closes the opening of the delivery spout D_1 for gas, but allows liquid to flow through a very narrow opening D_{111} along the gutter D_{13} . The first considerable quantities flowing from the cock, serve to cool all the beakers and the whole cryostat in the way indicated in Comm. 51 (the arrows of plate I might be borrowed from plate I of Comm. 51), unless the supply becomes so great that the valve D_{111} is opened and the gas also flows out through the opening R_{10} in the ring R_1 , plate II. The gas which later evaporates from the beaker B_{01} , finds the valve D_{111} closed and escapes only through the opening R_{10} , along the way indicated by the arrows on plate II, so that it serves only to screen the immediate neighbourhood of the bath from external heat.

The difference in form between the rings R_3 and R_4 on plate II and those on plate I Comm. 51 is very slight. This follows from the wish to use the parts that served in the experiments, referred to in

Comm. 51, as much as possible in the arrangement of the measuring apparatus considered here. Formerly the bath could be excentrically mounted with reference to the tube F_1 whereas this time a central mounting was desirable. The existing dimensions of parts of the apparatus have also had the result that in the experiments described here the bath must be placed a little too high with regard to the observing glasses V_2 , which might easily have been avoided if we had been perfectly free in our construction.

The glass ring R_6 , not occurring in the arrangement of Comm. 51, serves still better to screen the bath from external heat. Like the other beakers and glass cylinders B_1 , B_2 , B_3 , B_4 , B_{01} , B_{02} , it is silvered inside and outside, leaving open, however, vertical strips nearly corresponding in width with the resistance thermometer p .

The conical rim B_{01} lies loose on the beaker B_{01} . When the liquid boils up, it streams back to B_{01} along the wall of the funnel; if, however, B_{01} is filled to the brim and more liquid is poured in, this superfluous liquid flows over into the beaker B_{02} , which also is filled before a measurement is made. If an intense cooling of the neighbourhood of the bath is required, the beakers B_1 , B_2 , B_3 must also be filled. It should be remembered, however, that if this is done, the evaporation at low pressure, as long as liquid remains in the outer beakers, requires a powerful vacuum pump.

The bath itself only evaporates slowly. Instead of the double beakers B_{01} B_{02} we might take a vacuum glass in order to diminish the evaporation as has sometimes been done (comp. § 3). But it is not always easy to obtain vacuum glasses of the required dimensions and internally finished with the accuracy necessary for the proper working of the stirring apparatus. Moreover one will not be inclined to immerse delicate measuring apparatus in the bath before one is sufficiently certain that the vacuum glass will not burst as such of greater dimensions sometimes do.

§ 3. To make clear the purpose of the arrangements to be described in the next sections, it seems to me that the following particularisations will be useful. First of all the temperature gradient in the bath. Even when the liquid boils regularly we find that in the lower layers, as a result of the hydrostatic pressure, the temperature exceeds that of the upper layers. If, as often happens with greatly diminished pressures when boiling is not produced artificially, only evaporation at the surface occurs instead of boiling, the temperature in the upper layers of the bath may fall considerably below that of the lower. If then the liquid suddenly boils up, which always happens whenever

we do not stir vigorously, an unexpected change takes place in the distribution of the temperature in the bath and hence in the temperature of any measuring apparatus placed in it. In measurements of the kind considered here, we cannot allow such irregularities and fluctuations in the temperature of the bath, either as to time or place.

Of the various methods of preventing this sudden ebullition, the simplest is the generation of small bubbles of gas by means of the heat of a short resistance (boiling thread). If, however, there are ignitable gases among those successively introduced into the apparatus and if consequently an explosive mixture with air might be formed, this method is not without danger.

To bring about ebullition a current of gas is often led through the liquid, which, however, has the disadvantage of contaminating the evaporated gas. To avoid this difficulty I have led through the bath a current of the gas itself. This means was applied for instance to avoid the retardation in boiling in the vacuum vessel mentioned at the end of § 2, and also in order to cause a strong stirring in the bath by means of the current of gasbubbles. But this means also presents many difficulties, mostly arising from condensation phenomena in the delivery tube, or higher temperature of the gasbubbles; I therefore, preferred, the arrangement as described in § 4.

If the cryostat is used as it was intended to be in Comm. 51, the requirements for very accurate measurements would not be fulfilled, even though a uniform temperature throughout the bath was attained. There still remains a systematic regular rise of the temperature, because the gas used is never perfectly pure and the more permanent part evaporates first. In cases where measuring apparatus require longer to adopt the temperature of the bath than the time in which the temperature changes the amount permitted by the accuracy of the observation, we cannot reach more accurate results without additional means.

§ 4. We now pass on to the description of the arrangements which form the subject of this communication. The uniform temperature in the bath is obtained by stirring. The stirring apparatus is placed concentrically to the bath, thus leaving room in the most profitable way for the measuring apparatus. From this space the stirring apparatus (as in Comm. 27 May and June '96 Pl. III) is separated by a protecting cylinder ξ_0 (comp. the figure to the left of plate I). The upper ring χ_{01} is provided with small valves χ_{04} covering openings of the same form. If the stirring apparatus moves in the cylindrical space between ξ_0 and B_{02} the valves shut up

during the upward movement and open during the downward movement. The upward movement is brought about by means of the thin wires χ_1 , the downward movement by the weight of the stirring apparatus itself which for this purpose is weighted with the heavy ring χ_{02} by means of the rods χ_{03} . As yet a more rapid motion of the stirring apparatus than this method affords has not been required; if wanted a construction with small rods instead of threads would be necessary. The valves are hinged on bent pins χ_{041} . The complete section of the stirrer to the right of plate II shows the valves shut, the section of χ_{01} at the top shows them open. When the stirring apparatus is moved up and down and the bubbles of vapour escape the movements of the valves resemble those of the fins of fishes.

It is very important that the up and down motion of the ring should be perfectly perpendicular and that the protecting cylinder ξ_1 and the beaker B_{02} should have a perfectly vertical position for, to make the valves work properly, only a narrow space can be left between the stirrer and the cylindrical walls. The cylinder ξ_0 is enclosed between two rings provided with grooves ξ_1 and ξ_2 , of which the upper is connected with the ring ξ_3 by means of glass tubes. Through the operation of the spring ξ_{31} and the arch ξ_{30} , this ring is pressed against the ring ξ_4 on to which the beaker B_{02} with a ground upper rim is fastened by means of cords. To this ring ξ_4 the hooks ξ_7 are also fastened, against which the upper rim of the beaker B_{01} is also pressed by means of cords. In this way a cylindrical space is reserved for the pumping motion of the stirrer.

In order to admit the measuring apparatus it was advisable to leave free the whole space offered by tube F_1 , which is equal to that in the bath available for a measuring apparatus. To this end the threads χ_1 , formed of very thin silk cords enclosed in steel wire are led through 3 openings F_{31} in the cover F of the bath and then over a pulley axis χ_2 with three grooves to a connecting piece χ_3 , which is moved by a single thread passing over the pulleys χ_4 and χ_5 . The cord must be moved from outside the case and the case must remain perfectly air-tight. This is obtained by passing the cord through an india rubber tube χ_{41} , which at χ_{40} fits hermetically on to the cover of the cryostat and in which the thread χ_{42} is also hermetically fixed. A thin steel wire is wound spirally round the india rubber tube. In this way the walls of the tube offer sufficient resistance to the atmospheric pressure to prevent them from collapsing when low pressure exists in the cryostat, while at the same time

they remain elastic enough to permit the movements of the cord. A regular up and down motion of the stirring apparatus is secured by the wheel χ_7 .

§ 5. A constant temperature is attained by continually adjusting the pressure, at which the liquid in the bath evaporates, to the indications of a resistance thermometer ρ placed concentrically in the bath. A sensitive thermometer forms an inherent part of the cryostat under consideration when it is to be used for very constant temperatures and the dimensions allowing a resistance thermometer to be introduced, the latter has been chosen as the most trustworthy. Its inner diameter controls the greatest cross section of the measuring apparatus which can be immersed in the bath, and therefore, as in our case, it must correspond to that of the tube F_1 . The construction of this thermometer has been described in detail by B. MEILINK (Comm. 77 Febr. '02) with a view to a comparison between it and the hydrogen thermometer referred to above. The leads pass through the openings R_{30} , R_{40} of the ebonite rings R_3 and R_4 , and then through the stopper into the tube T_{11} . On the plates I and II they are indicated by the same letters as on the plate of Comm. 77.

When the bath has reached the required temperature the galvanometer in the WHEATSTONE'S bridge, which serves to measure the resistance of ρ , is adjusted to zero by introducing suitable resistances. As soon as the deviations of the galvanometer make it necessary, a sign is given to the assistant, charged with the regulation of the pressure in the cryostat, who then raises or diminishes the pressure, whereby the temperature in the bath rises or falls. The great volume of the cryostat is here very useful in checking oscillations in pressure. The arrangements required for the regulation of pressure are shown in plate I, the separate pieces of apparatus to scale and the connections schematically. (Comp. Comm. 51 Sept. '99, pl. IV). The assistant uses the oil manometer X_0 , which is connected to the cryostat by X_1 and X_2 (comp. pl. II Comm. 51) and the cock X_{90} , the cock X_{91} being open. If we shut the cock X_{91} the motion of the oil enables us to very accurately watch the variations of the pressure in the cryostat by means of the difference between the pressure in it and of the quantity of gas temporarily shut off in the reservoir X_{92} . If through some cause or other the variations of pressure increase considerably, or if we want to stop the regulation, or to proceed to another pressure, the oil is prevented from running over by our opening the cock X_{91} . The pressure in the cryostat is varied by more or less opening the fine cocks Y_{43} and Y_{42} of the regulation

tube Y_{41} . Two cases are to be distinguished here. With operations at ordinary pressure it will be sufficient to adjust the cryostat at a pressure a little higher than that of the atmosphere and to either connect the cock Y_{42} with a gasholder *Gas.* or to disconnect them, as the occasion demands. As soon as the pressure passes a certain limit settled for the cryostat, the gas escapes from the cryostat through the large safety apparatus. For operations at reduced pressure, the cryostat, after the pressure has been sufficiently lowered by means of the exhaustpump of the circulation *Ech.* 1, is disconnected from the latter and connected by means of the cock Y_{43} to the exhaustpump *Ech.* 2., and is then reduced to a lower pressure. Obviously we can sometimes avail ourselves for this latter operation of the same exhaustpump as used with *Ech.* 1. The evaporation will proceed more gradually when a connection is made to a reservoir at reduced pressure *Vac.*, plate. If a reservoir of large volume is used we can even work without an exhaustpump, which may be valuable when it is necessary to avoid vibration for the measurements. Thus with the bath of nitrogen under diminished pressure the auxiliary compressor of Comm. 54 Jan. '00 plate VII was connected near *Ech.* 1 to the gaslead and the vessel of 5 m³ mentioned above (comp. Comm. 14 Dec. '94 § 10) served as vacuum reservoir, after being exhausted through Y_{36} and Y_{37} by means of a BURCKHARDT vacuum pump, connected to the gaslead at *Ech.* 2. This vacuum pump will be described later.

In a few words we shall indicate the method which we usually follow in order to get a wellfilled bath at diminished-pressure. First the double beaker B_{01} , B_{02} , or several beakers B_1 , B_2 , B_3 are filled at ordinary pressure, then we begin to slowly exhaust through Y_{34} ; all other cocks being shut by means of the pump, generally used for the circulation *Ech.* 1; while boiling is prevented by rapidly moving the stirring apparatus described in § 4. When the required pressure is reached the cryostat is to be connected to the great reservoir *Vac.* at the same pressure. If this cannot be done we hardly ever succeed in admitting through the cock h_6 the yet required quantity of liquid slowly enough to keep the pressure in the cryostat free from undesirably large fluctuations or even to avoid with the help of Y_{36} momentarily returning of it to nearly its ordinary value. Therefore, if a change of temperature for some time is allowed, it is in that case better to shut Y_{34} before more liquid is added and to connect the cryostat through Y_{35} to the gasholder. As long as the beaker B_{02} is not full the gas leaving the cryostat is allowed to pass through Y_{35} into the gasholder. If the beaker B_{02} is full, which is shown by

the rise of the level in B_{01} , we once more begin to diminish the pressure (Y_{32} shut, Y_{34} open) which process generally takes some time. Then more liquid is admitted as before and if necessary this process is repeated several times. If the beaker is sufficiently filled at the desired reduced pressure we begin to regulate the pressure with the duly exhausted vacuum reservoir as described above.

Plate III shows a couple of graphical representations of the variations of the temperature of the bath. The ordinates show the deflections on the scale of the galvanometer in centimeters. The abscissae represent the time in minutes; fig. 1 relates to a measurement in methane at ordinary pressure; a deflection on the scale of 1 c.m. corresponds to about 0.009 deg. (the open space in the figure indicates a magnetic disturbance). Fig. 2 refers to oxygen at a diminished pressure; here a deflection on the scale of 1 c.m. corresponds to 0.005 deg. They were borrowed from the measurements of MEILINK mentioned above.

The temperature of the measurement is determined by the help of graphical representations, extending over the whole time of measurement, from which the portions reproduced on plate III have been taken. For this determination the readings of the galvanometer are noted down about twice every minute. By means of the planimeter we derive from the graphical representation obtained, the mean ordinate, which mean is considered as the temperature of the bath during the whole measurement.

(March 25, 1903).

Plate IV.

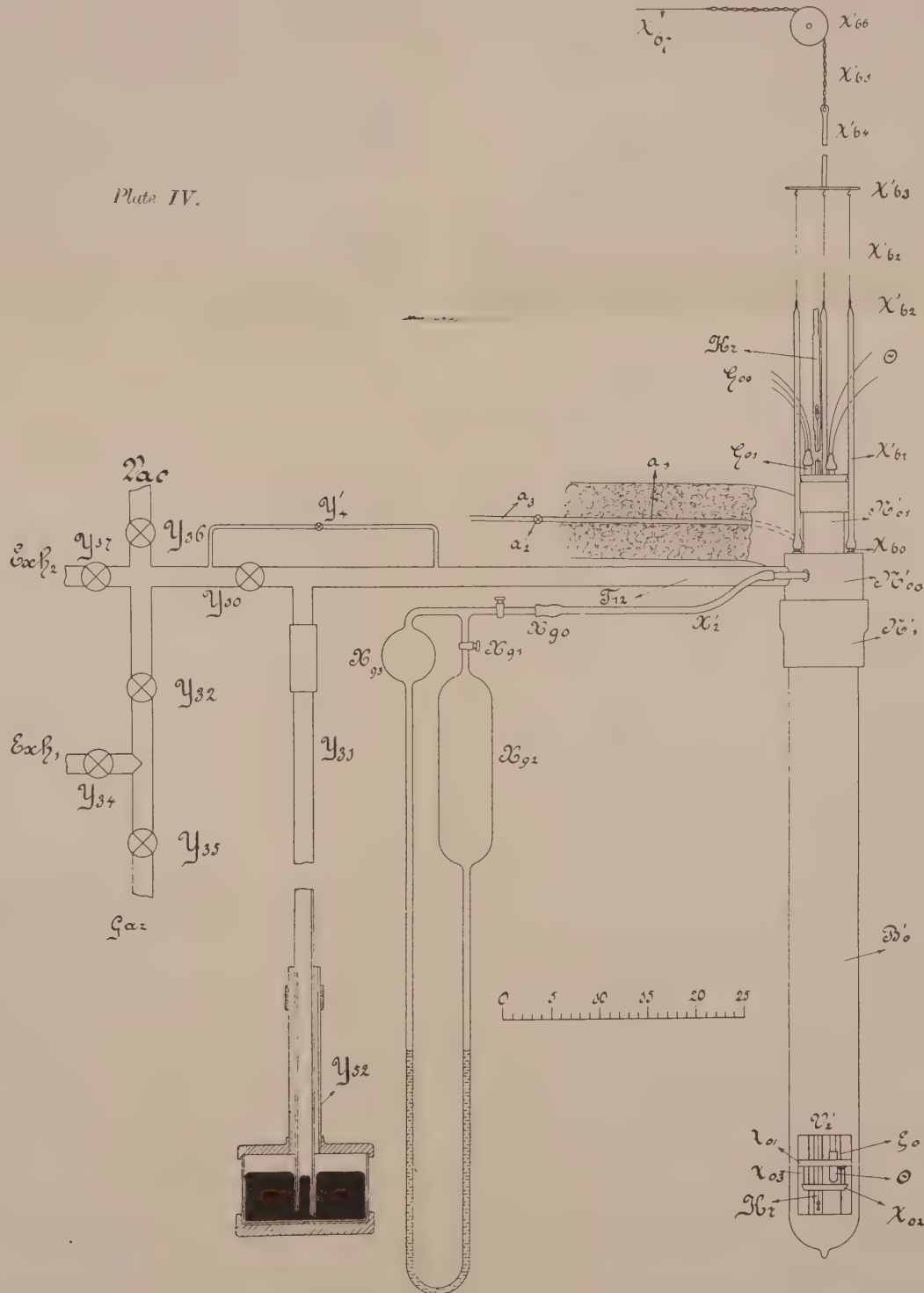
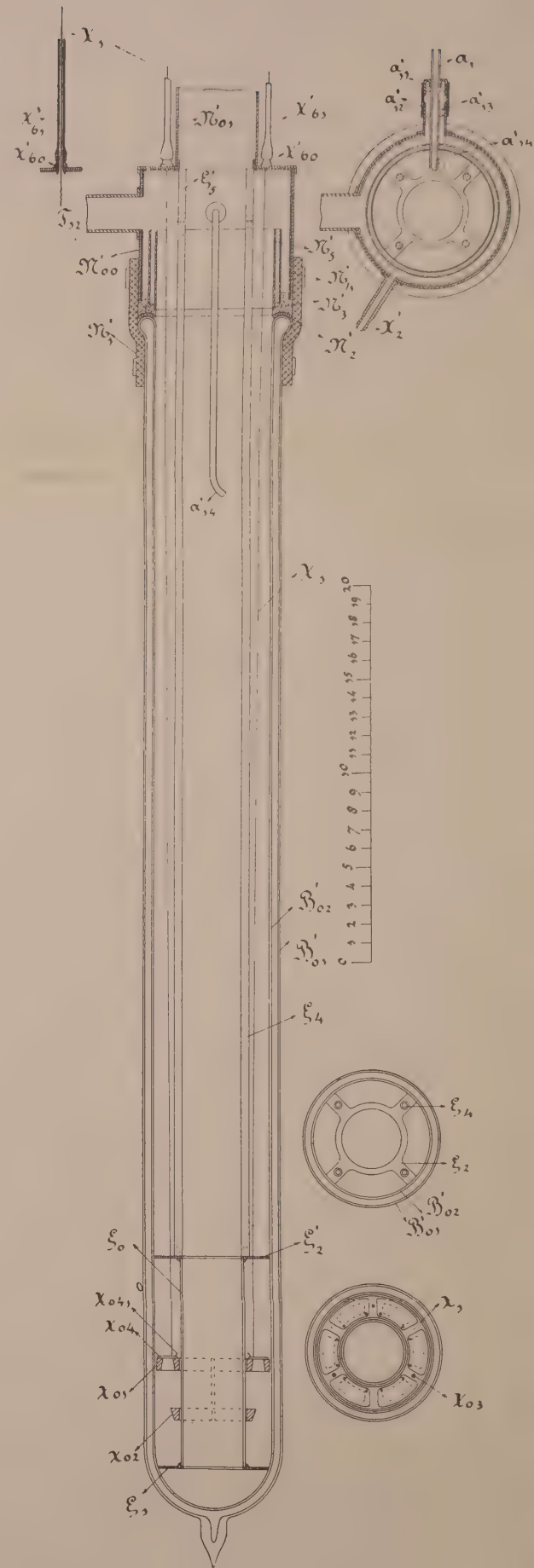
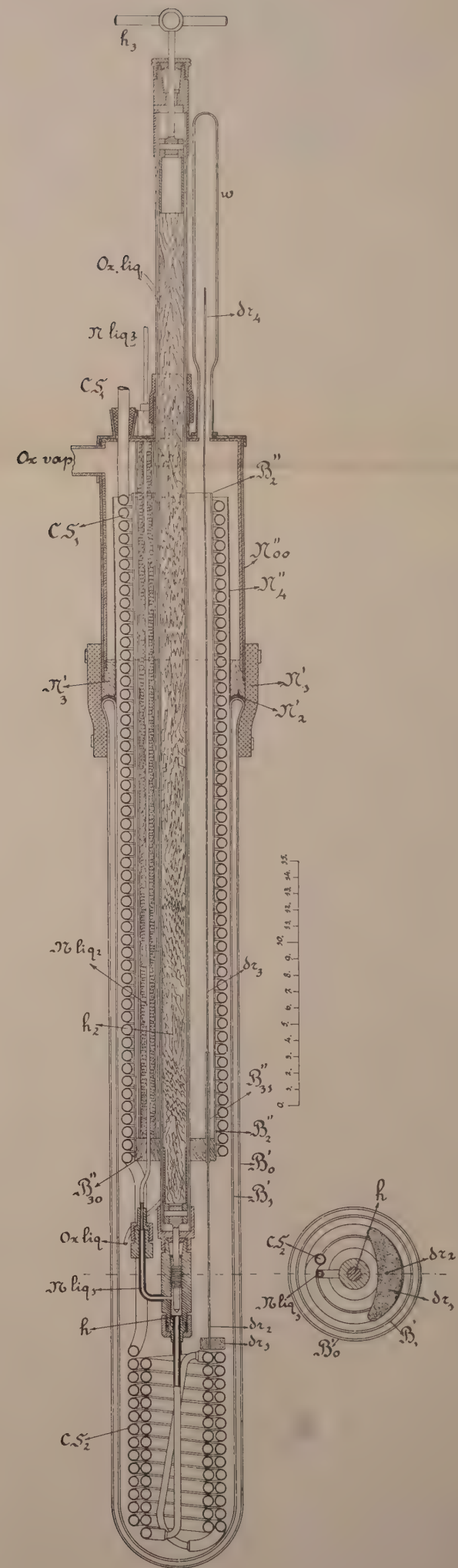


Plate V.



This technical drawing illustrates a complex steam engine and boiler system. The upper portion shows a boiler with various pipes, valves, and gauges, labeled with Cyrillic letters such as *В*, *В*₁, *В*₂, *В*₃, *В*₄, *В*₅, *В*₆, *В*₇, *В*₈, *В*₉, *В*₁₀, *В*₁₁, *В*₁₂, *В*₁₃, *В*₁₄, *В*₁₅, *В*₁₆, *В*₁₇, *В*₁₈, *В*₁₉, *В*₂₀, *В*₂₁, *В*₂₂, *В*₂₃, *В*₂₄, *В*₂₅, *В*₂₆, *В*₂₇, *В*₂₈, *В*₂₉, *В*₃₀, *В*₃₁, *В*₃₂, *В*₃₃, *В*₃₄, *В*₃₅, *В*₃₆, *В*₃₇, *В*₃₈, *В*₃₉, *В*₄₀, *В*₄₁, *В*₄₂, *В*₄₃, *В*₄₄, *В*₄₅, *В*₄₆, *В*₄₇, *В*₄₈, *В*₄₉, *В*₅₀, *В*₅₁, *В*₅₂, *В*₅₃, *В*₅₄, *В*₅₅, *В*₅₆, *В*₅₇, *В*₅₈, *В*₅₉, *В*₆₀, *В*₆₁, *В*₆₂, *В*₆₃, *В*₆₄, *В*₆₅, *В*₆₆, *В*₆₇, *В*₆₈, *В*₆₉, *В*₇₀, *В*₇₁, *В*₇₂, *В*₇₃, *В*₇₄, *В*₇₅, *В*₇₆, *В*₇₇, *В*₇₈, *В*₇₉, *В*₈₀, *В*₈₁, *В*₈₂, *В*₈₃, *В*₈₄, *В*₈₅, *В*₈₆, *В*₈₇, *В*₈₈, *В*₈₉, *В*₉₀, *В*₉₁, *В*₉₂, *В*₉₃, *В*₉₄, *В*₉₅, *В*₉₆, *В*₉₇, *В*₉₈, *В*₉₉, *В*₁₀₀. The lower portion shows a large steam engine with a flywheel, labeled with Cyrillic letters such as *В*, *В*₁, *В*₂, *В*₃, *В*₄, *В*₅, *В*₆, *В*₇, *В*₈, *В*₉, *В*₁₀, *В*₁₁, *В*₁₂, *В*₁₃, *В*₁₄, *В*₁₅, *В*₁₆, *В*₁₇, *В*₁₈, *В*₁₉, *В*₂₀, *В*₂₁, *В*₂₂, *В*₂₃, *В*₂₄, *В*₂₅, *В*₂₆, *В*₂₇, *В*₂₈, *В*₂₉, *В*₃₀, *В*₃₁, *В*₃₂, *В*₃₃, *В*₃₄, *В*₃₅, *В*₃₆, *В*₃₇, *В*₃₈, *В*₃₉, *В*₄₀, *В*₄₁, *В*₄₂, *В*₄₃, *В*₄₄, *В*₄₅, *В*₄₆, *В*₄₇, *В*₄₈, *В*₄₉, *В*₅₀, *В*₅₁, *В*₅₂, *В*₅₃, *В*₅₄, *В*₅₅, *В*₅₆, *В*₅₇, *В*₅₈, *В*₅₉, *В*₆₀, *В*₆₁, *В*₆₂, *В*₆₃, *В*₆₄, *В*₆₅, *В*₆₆, *В*₆₇, *В*₆₈, *В*₆₉, *В*₇₀, *В*₇₁, *В*₇₂, *В*₇₃, *В*₇₄, *В*₇₅, *В*₇₆, *В*₇₇, *В*₇₈, *В*₇₉, *В*₈₀, *В*₈₁, *В*₈₂, *В*₈₃, *В*₈₄, *В*₈₅, *В*₈₆, *В*₈₇, *В*₈₈, *В*₈₉, *В*₉₀, *В*₉₁, *В*₉₂, *В*₉₃, *В*₉₄, *В*₉₅, *В*₉₆, *В*₉₇, *В*₉₈, *В*₉₉, *В*₁₀₀. The drawing is a detailed technical illustration of a steam engine and boiler system, showing various components and their connections. The upper part of the drawing shows a boiler with a complex network of pipes, valves, and gauges. The lower part shows a large steam engine with a flywheel, connected to the boiler. The drawing is labeled with various Cyrillic and Latin letters, indicating different parts and components. The overall style is that of a technical drawing from the early 20th century.



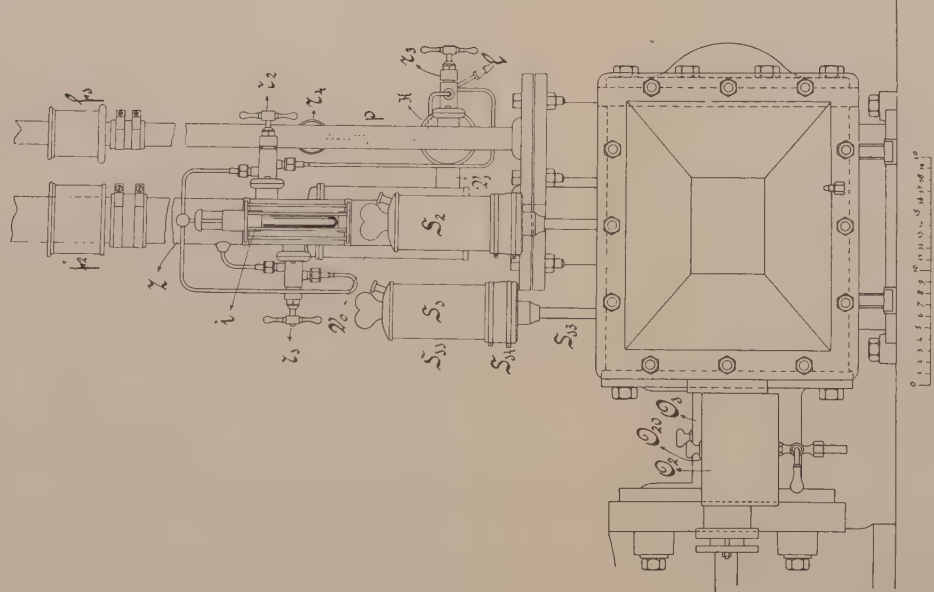


Fig. 1.

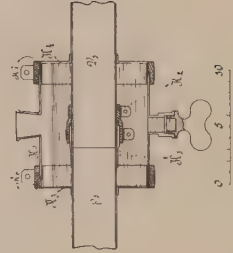
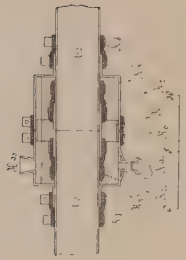
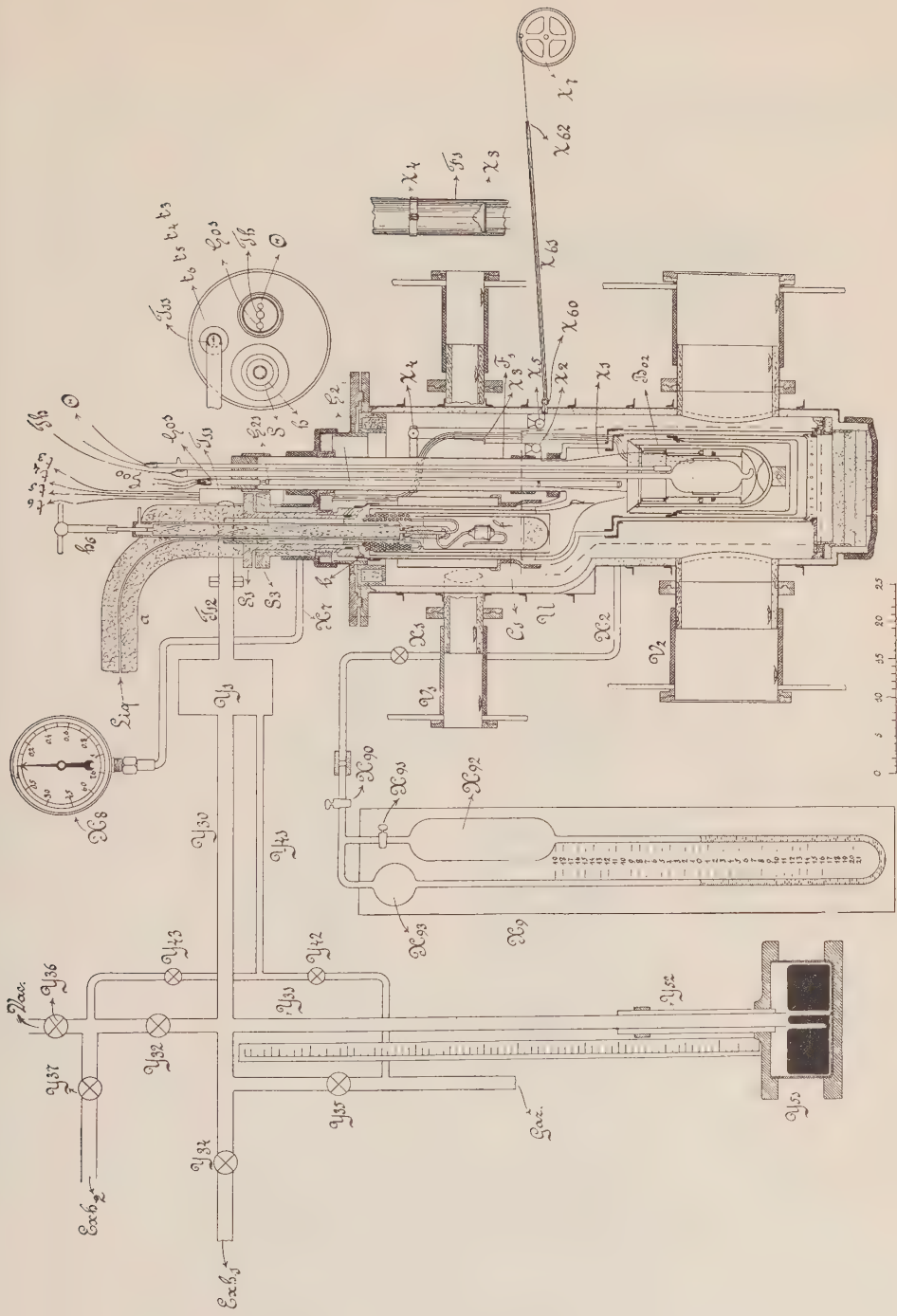


Fig. 5.





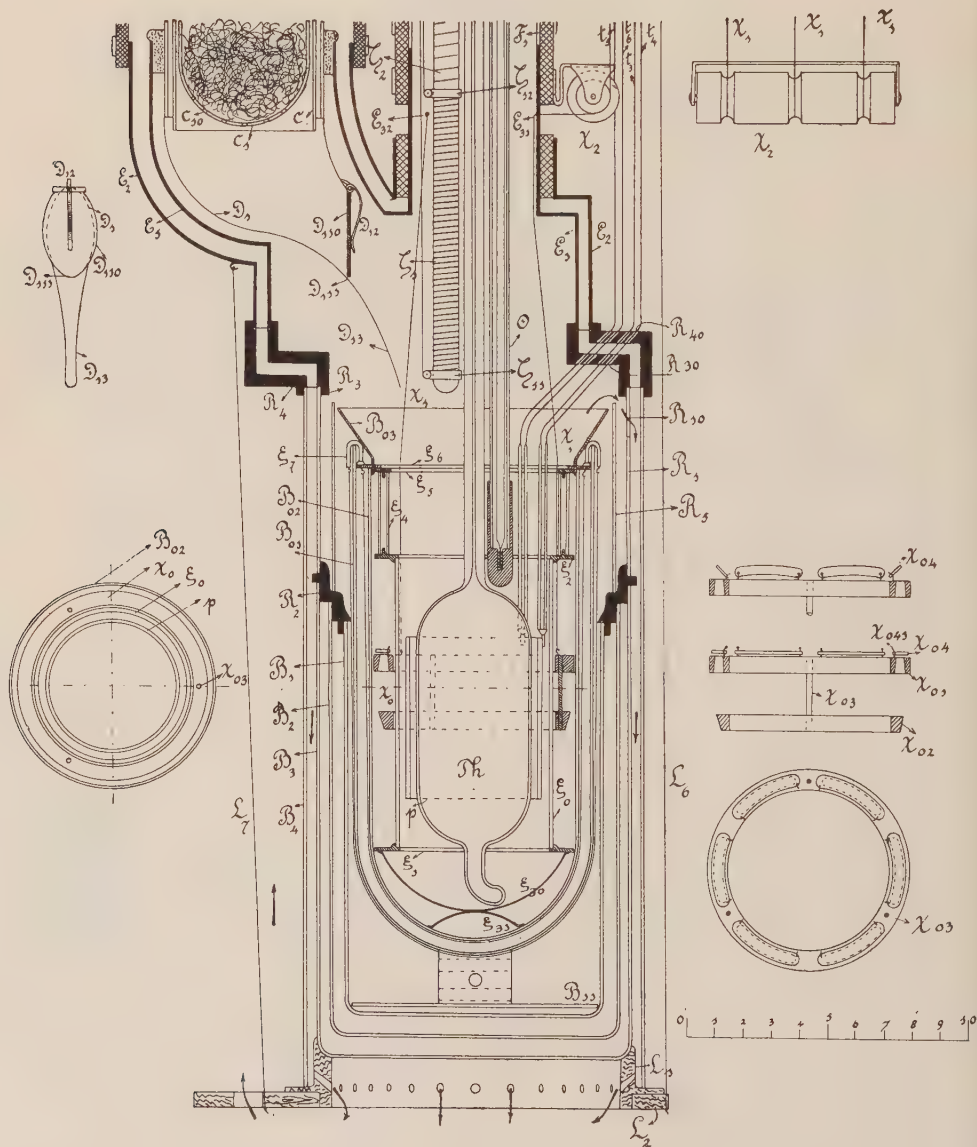
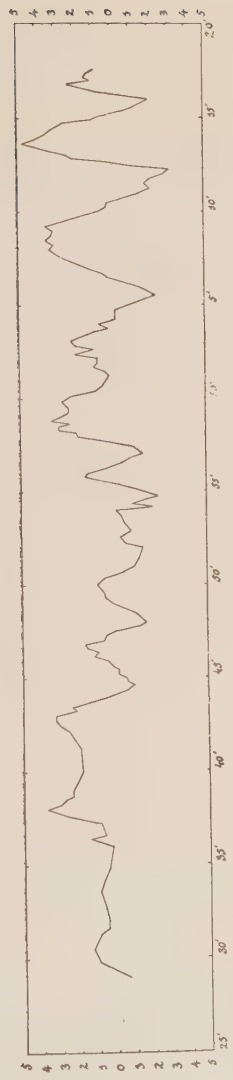


PLATE III.



KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN

TE AMSTERDAM.

PROCEEDINGS OF THE MEETING

of Saturday March 28, 1903.

(Translated from: Verslag van de gewone vergadering der Wis- en Natuurkundige Afdeeling van Zaterdag 28 Maart 1903, Dl. XI).

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H. KAMERLINGH ONNES: "Methods and apparatus used in the cryogenic Laboratory". III (continued) IV, V. p. 628.

H. KAMERLINGH ONNES and H. H. FRANCIS HYNDMAN: "Isotherms of diatomic gases and their binary mixtures. V. An accurate volumenometer and mixing apparatus", p. 636, (with 2 plates)

The following papers were read:

Chemistry. — "*The meltingpoint-line of Tin-Amalgams.*" By Dr. J. J. VAN LAAR. (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM). (2nd Communication).

(Communicated in the meeting of January 31, 1903).

1. In a previous communication (Proc. Dec. 1902) I showed, that when the molecular potential of tin in a liquid tin-amalgam is expressed by the formula

$$\mu_1 = f(T) + RT \log(1-x) + (\alpha_1 x^2 + \beta_1 x^3 + \dots),$$

a very good agreement is obtained between the *calculated* values of the melting-temperatures at various values of x , and the temperatures *observed* by VAN HETEREN (compare his Dissertation), at least up till about 80° C.

In a conference, I had since with prof. VAN DER WAALS, he called my attention to an expression for the correctionterm in μ_1 , which may be taken as a fairly good approximation¹⁾. This expression is:

$$\frac{\alpha_1 x^2}{(1 + nx)^2}.$$

After he had first shown (p. 193), that the correctionterm is really of the order x^2 — this I also showed in my previous communication, but in a different manner — and had observed, that (in the case investigated by him) the value of α_1 does not remain constant, but decreases when x increases (p. 198), he afterwards arrived at the said approximate expression (p. 213, 214), in agreement with an empirical relation of THOMSEN.

Though Prof. VAN DER WAALS has briefly given the deduction of his formula, it may be useful to state once more how this expression can be arrived at. The matter is of great importance, because the *same* quantity $\mu_1 - (\mu_1)_{x=0}$ constantly occurs in a great number of formulae, such as those for the lowering of the freezing-point, elevation of the boiling-point, alteration in vapour pressures, etc. If therefore this quantity is once for all accurately known, we may get a better insight into a great number of problems relating to binary mixtures.

2. As the *total* thermodynamic potential is represented by

$$\begin{aligned} \zeta = & - \sum (n_1 k_1) T (\log T - 1) + \left[\sum (n_1 (e_1)_0) - T \sum (n_1 (\eta_1)_0) \right] - \\ & - \left[\int p dV - pV \right] + RT \sum (n_1 \log n_1), \end{aligned}$$

we obtain for the *molecular* potential of the component n_1 :

$$\mu_1 = \frac{\partial \zeta}{\partial n_1} = -k_1 T (\log T - 1) + [(e_1)_0 - T(\eta_1)_0] - \left[\frac{\partial}{\partial n_1} \int p dV - p \frac{\partial V}{\partial n_1} \right] + RT + RT \log n_1.$$

With

$$p = \frac{\sum n_1 \cdot RT}{V - b} - \frac{a}{V^2}$$

¹⁾ Zeitschrift für Ph. Ch. 8, pg. 188 (1891). Also compare different passages in the second part of his "*Continuität*" on p. 43—45; 148; 152.

Recently, Prof. VAN DER WAALS has returned to this question in his "*Ternary Systems*" (Proc. March to July 1902). He gives there a more general and accurate expression, wherein occur the critical temperature and pressure of the mixture (Compare in particular IV, p. 92—96).

we find :

$$\int p dV = \Sigma n_1 \cdot RT \log (V-b) + \frac{a}{V},$$

and therefore

$$\frac{\partial}{\partial n_1} \int p dV = RT \log (V-b) + \frac{\Sigma n_1 \cdot RT}{V-b} \frac{\partial (V-b)}{\partial n_1} - \frac{a}{V^2} \frac{\partial V}{\partial n_1} + \frac{1}{V} \frac{\partial a}{\partial n_1}.$$

Deducting from this :

$$p \frac{\partial V}{\partial n_1} = \left[\frac{\Sigma n_1 \cdot RT}{V-b} - \frac{a}{V^2} \right] \frac{\partial V}{\partial n_1},$$

we get :

$$\frac{\partial}{\partial n_1} \int p dV - p \frac{\partial V}{\partial n_1} = RT \log (V-b) - \frac{\Sigma n_1 \cdot RT}{V-b} b_1 + \frac{2}{V} (n_1 a_1 + n_2 a_{12}).$$

Substituting $a = n_1^2 a_1 + 2 n_1 n_2 a_{12} + n_2^2 a_2$ for a , and the linear relation $b = n_1 b_1 + n_2 b_2$ for b in the case of *two* components, the expression for μ_1 becomes :

$$\begin{aligned} \mu_1 = & -k_1 T (\log T - 1) - RT (\log (V-b) - 1) + [(e_1)_0 - T(\eta_1)_0] + \\ & + \frac{\Sigma n_1 \cdot RT}{V-b} b_1 - \frac{2}{V} (n_1 a_1 + n_2 a_{12}) + RT \log n_1, \quad . \quad . \quad . \quad . \quad . \quad (1) \end{aligned}$$

in agreement with what I wrote down in my first communication.

If now we write $n_1 = 1-x$, $n_2 = x$, this then becomes :

$$\begin{aligned} \mu_1 = & -k_1 T (\log T - 1) - RT (\log (V-b) - 1) + [(e_1)_0 - T(\eta_1)_0] + \\ & + \frac{RT b_1}{V-b} - \frac{2}{V} [(1-x) a_1 + x a_{12}] + RT \log (1-x). \end{aligned}$$

For the determination of the complete function of x , which occurs here outside $RT \log (1-x)$, we will now determine the value of

$$\frac{RT b_1}{V-b} - \frac{2}{V} [(1-x) a_1 + x a_{12}].$$

The term with $\log (V-b)$ is supposed to be but very little dependent on x in regard to these two. If in the equation of condition we put $p = 0$, which is certainly permissible in the case of liquid phases,

then $\frac{RT}{V-b}$ may be replaced by $\frac{a}{V^2}$, and the above expression becomes :

$$\frac{((1-x)^2 a_1 + 2 x (1-x) a_{12} + x^2 a_2) b_1}{V^2} - \frac{2 ((1-x) a_1 + x a_{12})}{V}.$$

If now we replace V by b , which will hold for liquids at low temperatures in approximation, we obtain :

$$\frac{((1-x)^2 a_1 + 2x(1-x)a_{12} + x^2 a_2) b_1 - 2((1-x)a_1 + x a_{12})(1-x)b_1 + x b_2}{b^2},$$

or :

$$\frac{-a_1((1-x)^2 b_1 + 2x(1-x)b_2) - 2a_{12}x^2 b_2 + a_2 x^2 b_1}{b^2},$$

which we may also write as

$$-\frac{a_1}{b_1} + \frac{a_1 b_2^2 - 2a_{12} b_1 b_2 + a_2 b_1^2}{b_1 b^2} x^2.$$

We therefore finally and approximately obtain :

$$\mu_1 = -k_1 T(\log T - 1) - RT(\log(V_1 - b_1) - 1) + [(e_1)_0 - T(\eta_1)_0] - \frac{a_1}{b_1} + \frac{A}{b_1} \frac{x^2}{b^2} + RT \log(1-x),$$

when we call

$$a_1 b_2^2 - 2a_{12} b_1 b_2 + a_2 b_1^2 = A.$$

The corresponding expression for μ_2 evidently becomes :

$$\mu_2 = -k_2 T(\log T - 1) - RT(\log(V_2 - b_2) - 1) + [(e_2)_0 - T(\eta_2)_0] - \frac{a_2}{b_2} + \frac{A}{b_2} \frac{(1-x)^2}{b^2} + RT \log x.$$

As (omitting p) it follows from the equation of condition, that

$$V - b = \frac{RTV^2}{a} = \frac{RTb^2}{a},$$

and that, therefore, $\log(V_1 - b_1) = \log \frac{Rb_1^2}{a_1} + \log T$, we may write in general :

$$\left. \begin{aligned} \mu_1 &= e_1 - c_1 T - (k_1 + R) T \log T + a_1 \frac{x^2}{(1+rx)^2} + RT \log(1-x) \\ \mu_2 &= e_2 - c_2 T - (k_2 + R) T \log T + a_2 \frac{(1-x)^2}{(1+rx)^2} + RT \log x \end{aligned} \right\} \quad (2)$$

In this equation then

$$e_1 = (e_1)_0 - \frac{a_1}{b_1}; \quad e_2 = (e_2)_0 - \frac{a_2}{b_2}$$

$$c_1 = (\eta_1)_0 - (k_1 + R) + R \log \frac{Rb_1^2}{a_1}; \quad c_2 = (\eta_2)_0 - (k_2 + R) + R \log \frac{Rb_2^2}{a_2},$$

whilst

$$\frac{A}{b_1^3} = \alpha_1 \quad \text{and} \quad \frac{A}{b_2 b_1^2} = \alpha_2,$$

and also

$$\frac{-b_1 + b_2}{b_1} = r.$$

Remark. The quantity $\mu_1 = \frac{\partial \xi}{\partial n_1}$ may also be obtained by the operation $\mu_1 = \xi - x \frac{\partial \xi}{\partial x}$. For the term $-\int p dV + pV$, occurring in ξ , may be written $-\int p dV = -RT \log(V-b) - \frac{a}{V}$. The required function of x may therefore also be found by calculating ($V=b$,

$$-\left(\frac{a}{b} - x \frac{\partial}{\partial x} \left(\frac{a}{b}\right)\right),$$

for which we then find exactly in the same way as above:

$$-\frac{a_1}{b_1} + \frac{a_1 b_2^2 + a_2 b_1^2 - 2a_{12} b_1 b_2}{b_1 b^3} x^2.$$

The two methods of calculation are, of course, identical. The last has the advantage, that we see at once that the differential coefficient of the correction term of x , i. e. $\frac{2A_2 x}{b^3}$, is nothing but $x \frac{\partial^2}{\partial x^2} \left(\frac{a}{b}\right)$, so that we have:

$$\frac{1}{x} \frac{\partial \mu'_1}{\partial x} = -\frac{1}{1-x} \frac{\partial \mu'_2}{\partial x} = -\frac{\partial^2 \xi'_1}{\partial x^2} = \frac{\partial^2}{\partial x^2} \left(\frac{a}{b}\right) = \frac{2A}{b^3},$$

when ξ' , μ'_1 and μ'_2 represent the quantities ξ , μ_1 and μ_2 with omission of the terms containing $\log(1-x)$ and $\log x$. As regards the quantity $\mu_2 = \frac{\partial \xi}{\partial x}$, we must remember, that this is also obtained from the relation

$$\mu_2 = \xi + (1-x) \frac{\partial \xi}{\partial x}.$$

3. It is now the question, whether the expression

$$\alpha_1 \frac{x^2}{(1+rx)^2}$$

represents the melting-points of the tin-amalgams as well as, or better than my semi-empirical expression

$$\alpha_1 x^2 + \beta_1 x^3 + \gamma_1 x^4.$$

Let us first observe, that VAN DER WAALS always found α_1 *negative* in the case of electrolytes and other aqueous solutions (l. c. p. 195). Now it is evident, that if we may write $a_{12} = \sqrt{a_1 a_2}$, the coefficient

α_1 becomes $\frac{(b_2 \sqrt{a_1} - b_1 \sqrt{a_2})^2}{b_1^3}$, and ought therefore to be always found

positive. (I found for instance α_1 *positive* with tin-amalgams). It therefore seems, that when one of the components (water for instance) is an *associating* substance, or when the other component is *electrolytically dissociated*, we must certainly *not* follow D. BERTHELOT in writing $a_1 a_2 = a_{12}^2$, independent of the fact, that in such cases neither a_1 and a_2 , nor b_1 and b_2 are constants.

The formule (8) in my previous communication now becomes:

$$T = T_0 \frac{1 + \frac{1}{q_0} \frac{\alpha_1 x^2}{(1+rx)^2}}{1 - \frac{RT_0}{q_0} \log(1-x)},$$

$$\text{or with } \frac{\alpha_1}{q_0} = \alpha, \quad \frac{RT_0}{q_0} = \theta:$$

$$T = T_0 \frac{1 + \frac{\alpha x^2}{(1+rx)^2}}{1 - \theta \log(1-x)}. \quad \dots \quad (8bis)$$

From observations, where the values of x are less than 0,1, the value of θ was found to be exactly 0,396¹⁾. If we now further accept for the values of the coefficients α and r :

$$\alpha = 0,0453; \quad r = -0,74,$$

which are calculated from other observations with higher values of x , we obtain ($T_0 = 273,15 + 231,63 = 504,8$) the survey on the next page.

We notice, that in this table the agreement is an excellent one; the average deviation is about 0,9°, whilst in the case of the empirical formula with βx^2 and γx^3 (see previous communication), if the last value is not counted, it amounted to 0.85°. VAN DER WAALS's expression for the correctionterm, therefore, represents at least equally well the course of the meltingpoint-line over the portion, observed from 212° to 65°. But what is still more important, is the fact, that whilst my former empirical formula does not very accurately represent the two last observations (the difference in the last even amounted to 10°), VAN DER WAALS's expression not only satisfactorily represents these, but also the four observations at still lower temperatures (compare p. 22 of VAN HETEREN's Dissertation). In this observations the values of x and t were determined by analysis of the liquid phase, which is in equilibrium with the solid phase at a given temperature.

¹⁾ In the previous communication 0.400 was accepted, but $\frac{200}{505} = 0,396$ is somewhat more accurate.

x	x^2	Denom. $1-\theta \log (1-x)$	αx^2	$(1+rx)^2$	Numerat. $1+\frac{\alpha x^2}{(1+rx)^2}$	$T-273^{\circ}.15$ calculated	id. found	Δ
0.1005	0.0101 ⁰	1.0420	0.00045 ⁸	0.8567	1.0005	211.6	211.6	0
0.1716	0.0294 ⁵	1.0745	0.00133 ⁴	0.7621	1.0018	197.5	198.6	-1.1
0.2338	0.0546 ⁶	1.1054	0.00247 ⁶	0.6839	1.0036	185.2	183.7	+1.5
0.2969	0.0881 ⁵	1.1395	0.00399 ³	0.6089	1.0066	172.8	173.0	-0.2
0.3856	0.1487	1.1930	0.00673 ⁶	0.5108	1.0132	155.6	155.2	+0.4
0.5001	0.2501	1.2745	0.01133	0.3968	1.0286	134.3	133.4	+0.9
0.5973	0.3568	1.3602	0.01616	0.3114	1.0519	117.3	115.2	+2.1
0.6467	0.4182	1.4119	0.01894	0.2719	1.0697	109.3	107.4	+1.9
0.6754	0.4562	1.4456	0.02067	0.2502	1.0826	105.0	103.4	+1.6
0.6813	0.4642	1.4528	0.02103	0.2458	1.0856	104.0	102.4	+1.6
0.7104	0.5047	1.4907	0.02286	0.2250	1.1016	99.9	99.0	+0.9
0.7155	0.5119	1.4978	0.02319	0.2214	1.1048	99.2	98.8	+0.4
0.7477	0.5591	1.5454	0.02533	0.1995	1.1270	95.0	95.4	-0.4
0.7547	0.5696	1.5565	0.02580	0.1949	1.1324	94.1	94.0	+0.1
0.7963	0.6341	1.6301	0.02873	0.1687	1.1703	89.3	90.0	-0.7
0.8189	0.6706	1.6767	0.03038	0.1552	1.1957	86.8	88.4	-1.6
0.8921	0.7958	1.8817	0.03605	0.1155	1.3121	78.9	79.7	-0.8
0.9483	0.8993	2.1731	0.04074	0.0889 ⁸	1.4579	65.5	65.2	+0.3

x	x^2	Denom.	αx^2	$(1+rx)^2$	Numerat.	$T-273^{\circ}.15$ calculated	id. found	Δ
0.9879	0.9759	2.7482	0.04421	0.0723 ¹	1.6114	22.9	25.0	-2.1
0.9903	0.9807	2.8357	0.04443	0.0714 ⁰	1.6223	15.7	15.0	+0.7
0.9941	0.9882	3.0326	0.04477	0.0699 ¹	1.6403	— 0.1	0.0	-0.1
0.9964	0.9928	3.2282	0.04497	0.0690 ¹	1.6516	— 14.9	-18.8	+3.9

The agreement is even unexpectedly great, when we consider, that the meltingpoint-line runs here almost vertical, and a quite insignificant change in x causes a difference of several degrees in T .

4. Let us examine the formula

$$T = T_0 \frac{1 + 0,0453 \left(\frac{x}{1 - 0,74 x} \right)^2}{1 - 0,396 \log(1 - x)}$$

more closely. With small values of x it passes into

$$T = T_0 \frac{1 + 0,0453 x^2}{1 + 0,396 (x + \frac{1}{2} x^2)} = T_0 [1 - 0,396 x + 0,004 x^2].$$

Because the coefficient of x^2 is *accidentally* nearly 0, the melting-point-line in this case runs over a fairly large region (from 232° to 120°) as an almost *straight line*. To ensure this, it is generally necessary, that $0^2 - \frac{1}{2} 0 + a$ is very small or 0.

As, for equilibrium between the solid tin and the tin in the amalgam, $\mu = \mu_1$ or

$$-\mu + \mu_1 = 0,$$

we also have:

$$\frac{\partial}{\partial T}(-\mu + \mu_1) + \frac{\partial}{\partial x}(-\mu + \mu_1) \frac{dx}{dT} = 0.$$

Now according to a well-known theorem $\frac{\partial}{\partial T}(-\mu + \mu_1) = -\frac{q}{T}$.

The molecular potential μ for the solid phase is moreover not dependent on x . Therefore:

$$-\frac{q}{T} + \frac{\partial \mu_1}{\partial x} \frac{dx}{dT} = 0,$$

and consequently

$$\frac{dT}{dx} = \frac{T}{q} \frac{\partial \mu_1}{\partial x}.$$

We therefore see, that supposing the solid phase (as in this case) contains no mercury, $\frac{dT}{dx}$ cannot become 0, unless $\frac{\partial \mu_1}{\partial x} = 0$. But then the liquid phase will be *unstable*, and we find ourselves on the spinodal line, so that the liquid amalgam would long ago have broken up into two phases of different composition.

Now, $\frac{\partial \mu_1}{\partial x}$ and therefore also $\frac{dT}{dx}$ may become zero in the case of *two* values for x ; there are therefore in this case always two horizontal tangents. A limiting case of this is of course a point of inflection with only one horizontal tangent.

As

$$\frac{d^3T}{dx^3} = \frac{T}{q} \frac{\partial^2 \mu_1}{\partial x^2} + \frac{\partial \mu_1}{\partial x} \frac{d}{dx} \left(\frac{T}{q} \right),$$

this limiting case will evidently occur when

$$\frac{\partial \mu_1}{\partial x} \quad \text{and} \quad \frac{\partial^2 \mu_1}{\partial x^2}$$

are 0 at the same time. Now

$$\frac{\partial \mu_1}{\partial x} = -\frac{RT}{1-x} + \frac{2A}{b_1^3} \frac{x}{(1+rx)^3}; \quad \frac{\partial^2 \mu_1}{\partial x^2} = -\frac{RT}{(1-x)^2} + \frac{2A}{b_1^3} \frac{1-2rx}{(1+rx)^4},$$

so that for this point of inflection we shall have the relations

$$\frac{x(1-x)}{(1+rx)^3} = \frac{RT}{2\alpha_1}; \quad \frac{(1-x)^2(1-2rx)}{(1+rx)^4} = \frac{RT}{2\alpha_1}.$$

On dividing, we find :

$$x(1+rx) = (1-x)(1-2rx),$$

or

$$rx^2 - 2(1+r)x + 1 = 0.$$

When r is either negative or positive, we find from this :

$$x_c = \frac{1+r - \sqrt{1+r+r^2}}{r}, \quad . \quad . \quad . \quad . \quad . \quad (a)$$

when x_c indicates the value of x at the point of inflection. x_c may run from $1/2$ (if $r=0$) to 1 (if $r=-1$), when r is *negative*. If, however, r is *positive*, x_c runs from $1/2$ (if $r=0$) to 0 (if $r=\infty$). The positive sign for $\sqrt{1+r+r^2}$ would give in both cases impossible values for x_c .

We now further obtain :

$$\frac{x_c(1-x_c)}{(1+rx_c)^3} = \frac{RT}{2\alpha q_0} = \frac{RT_0}{q_0} \cdot \frac{1}{2\alpha} \cdot \frac{T}{T_0} = \frac{\theta}{2\alpha} \cdot \frac{T}{T_0},$$

that is to say, when for $\frac{T}{T_0}$ is substituted its value from (8bis) :

$$\frac{x_c(1-x_c)}{(1+rx_c)^3} \begin{matrix} \geq \\ < \end{matrix} \frac{\theta}{2\alpha} \cdot \frac{1 + \frac{\alpha x_c^2}{(1+rx_c)^2}}{1 - \theta \log(1-x_c)},$$

where the lower sign indicates conditions, where $\frac{\partial \mu_1}{\partial x} < 0$, and which are consequently *stable*. From this then follows :

$$2\alpha \frac{x_c(1-x_c)}{1+rx_c} (1 - \theta \log(1-x_c)) \begin{matrix} \geq \\ < \end{matrix} \theta [(1+rx_c)^2 + \alpha x_c^2].$$

Now, from the equation, from which (a) was deduced, we find:

$$1 + r x_c = 3 \frac{1 - x_c}{2 - x_c},$$

so that also

$$\frac{2}{3} \alpha x_c (2 - x_c)^3 (1 - \theta \log (1 - x_c)) \leq \theta [9 (1 - x_c)^2 + \alpha x_c^2 (2 - x_c)^2],$$

consequently

$$\alpha \leq \frac{27\theta(1-x_c)^2}{x_c(2-x_c)^2[2(2-x_c)(1-\theta \log(1-x_c))-3\theta x_c]} \quad . \quad . \quad (b)$$

If, therefore, $\alpha =$ or $>$ than this value, then $\frac{\partial \mu_1}{\partial x}$ becomes 0 on one or two places on the meltingpoint-line.

From the expression for $\frac{\partial \mu_1}{\partial x}$ (see above) it follows immediately, that when A , and consequently α , should be *negative*, $\frac{\partial \mu_1}{\partial x}$ can never become 0, still less positive. The occurrence of *unstable* conditions on the meltingpoint-line may, therefore, only be expected in the case of *positive* α , and only then, as soon as α reaches or exceeds the value, given by (b).

The relations (a) and (b), when united, give therefore the condition for *stable* phases along the *entire* meltingpoint-line.

In our example $r = -0.74$, and (a) gives $x_c = 0.863$. The equation (b) further gives with $\theta = 0.396$:

$$\alpha \leq \frac{27 \times 0.396 \times (0.137)^2}{0.863 \times (1.137)^2 [2 \times 1.137 (1 - 0.396 \log 0.137) - 3 \times 0.396 \times 0.863]},$$

that is to say

$$\alpha \leq \frac{0.180}{2.274 \times 1.787 - 1.025} \quad \text{or} \quad \alpha \leq \frac{0.180}{3.04} \quad \text{or} \quad \alpha \leq 0.0592.$$

Now, in our case α was 0.0453, so that everywhere we find ourselves in the stable region (as may in fact be seen from the shape of the observed meltingpoint-line). If α had been 0.059, we should have had a point of inflection with horizontal tangent; and had α been 0.059, we should have noticed the occurrence of a horizontal tangent in two places of the meltingpoint-line. This last case is, of course, not realisable, as the liquid amalgam would break up into two heterogenous liquid phases of different composition.¹⁾

¹⁾ It is perhaps not devoid of importance to observe, that when the *solid* phase forms a *solid solution* of the two components, the presence in the meltingpoint-line of a point of inflection with a *horizontal* tangent points as before to *unstable* conditions. For in the general relation

Another question is, at what values of x and T does $\frac{\partial \mu_1}{\partial x}$ first become 0, or where does the plait commence, independent of the fact whether we find ourselves on the meltingpoint-line or not, which had just been investigated.

We have only to combine the relations $\frac{\partial \mu_1}{\partial x} = 0$ and $\frac{\partial^2 \mu_1}{\partial x^2} = 0$

$$\frac{dT}{dx} = T \frac{(x_2 - x_1) \frac{\partial^2 \xi_1}{\partial x_1^2}}{w_{21}}$$

$\frac{dT}{dx}$ always becomes 0 in *one* place only in consequence of $x_2 - x_1$ becoming 0,

whilst on account of $\frac{\partial^2 \xi_1}{\partial x^2}$ becoming 0, $\frac{dT}{dx}$ always becomes 0 in *two* places, or

in the limiting case in *two coinciding* places in a point of inflection with a horizontal tangent. DE VISSER thinks he has found such a point of inflection with mixtures of stearic and palmitic acids.¹⁾ It is, of course, not impossible, that we are dealing here accidentally with a case, in which the quantity α possesses the value indicated by (b). That the line of the end-solidifyingpoints also shows in the immediate neighbourhood a similar point of inflection, points to the fact, that the

conditions $\frac{\partial^2 \xi}{\partial x^2} = 0$, $\frac{\partial^2 \xi}{\partial x^3} = 0$ are fulfilled on both lines at about *the same time*,

which renders it more accidental still, because x would then possess the value required for this also in the *solid* phase. It should be pointed out, that as a rule

the conditions $\frac{\partial^2 \xi}{\partial x^2} = 0$, $\frac{\partial^2 \xi}{\partial x^3} = 0$ for *both* phases by no means include $x_1 = x_2$. For

this requires $\frac{\partial \xi_1}{\partial x_1} = \frac{\partial \xi_2}{\partial x_2}$. It is therefore a new accident, that both points of

inflection appear to coincide. But for this a reason may be given here. From the equation, from which (a) is found, namely $rx^2 - 2(1+r)x + 1 = 0$, it follows that with $r = 0$, $x = 1/2$. DE VISSER now found both points of inflection to be at x about $1/2$ ($= 0.525$), so that the quantity r , both in the solid and liquid phase, is about 0 ($b_1 = b_2$). And in that case the values of x at both points of inflection *must* agree, namely both at $x = 1/2$.

The case, studied by DE VISSER, *may* therefore be an accidental coincidence of

the two points of inflection. But then, on account of $\frac{\partial^2 \xi_1}{\partial x_1^2} = 0$ and $\frac{\partial^2 \xi_2}{\partial x_2^2} = 0$, both

the *liquid* and *solid* phases must have broken up into two layers, although of *identical* composition. The smallest delay in solidification would however immediately have carried the system within the plait, and then both phases would have broken up into two layers of a *somewhat differing* composition. It is however more probable, that both lines *nearly* show a point of inflection with a horizontal tangent, and that they *approach very near*, but *not touch* each other.

¹⁾ Rec. Trav. Chim. (2) T. 2, N^o. 2 and 4 (1898).

to find the values of x and T at the "critical" point. We find as above :

$$x_c = \frac{1+r-\sqrt{1+r+r^2}}{r} \quad . \quad . \quad . \quad . \quad . \quad . \quad (3a)$$

The temperature T_c of this critical point is found from $\frac{\partial \mu_1}{\partial x} = 0$, that is to say from

$$\frac{x_c(1-x_c)}{(1+rx_c)^3} = \frac{\theta}{2\alpha} \frac{T_c}{T_0}.$$

We consequently find :

$$T_c = T_0 \frac{2\alpha}{\theta} \frac{x_c(1-x_c)}{(1+rx_c)^3},$$

$$\text{or, as } 1+rx_c = 3 \frac{1-x_c}{2-x_c} :$$

$$T_c = \frac{1}{27} T_0 \cdot \frac{2\alpha}{\theta} \frac{x_c(2-x_c)^3}{(1-x_c)^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (3b)$$

At this, or at lower temperatures, $\frac{\partial \mu_1}{\partial x}$ being then positive, we find ourselves therefore in the plait.

In the case of tin and mercury we find for x_c the value 0,863 (see above), if $r = -0,74$. For T_c we find :

$$T_c = \frac{504,8}{27} \times \frac{0,0906}{0,396} \times 67,60 = 289^{\circ}2.$$

The "critical" point is therefore situated at 16° C., that is to say fully 57° lower than the point of the meltingpoint-line, belonging to $x = 0,863$ (13,7 atom-percent tin), namely $83^{\circ}2$ C.

There are of course cases, where that distance is smaller, and where consequently a trifling supercooling already carries us within the region of the plait, which then — in the absence of the solid phase — causes a separation into two layers.

I may observe, that the value x_c does not correspond as a rule with a point of inflection (with oblique tangent) on the meltingpoint-line, when the critical point is not situated *on* the meltingpoint-line. For $\frac{\partial \mu_1}{\partial x} = 0$, $\frac{\partial^2 \mu_1}{\partial x^2} = 0$ do not lead to $\frac{d^2 T}{dx^2} = 0$, when these differential-coefficients do not become 0 *on* the meltingpoint-line.

5. The value of q , the heat of fusions of tin in the liquid amalgam, is evidently :

$$q = q_0 \left(1 + \frac{\alpha x^2}{(1+rx)^2} \right).$$

When the value of x is small, and assuming, that mercury dissolved in tin is *monatomic*, we find for q_0 by calculation 2550 gram-cals. PERSON found experimentally 1690 gram-cals. Should this figure be confirmed, it would prove, that the associationfactor of mercury is about 1.5.

Now, it follows from the above formula, that at 25° , where x is about 1, q ought to be

$$= 2550 \times 1,6114 = 4110 \text{ gram-cals.},$$

whilst VAN HETEREN, by electromotive measurements, found about 3000 gram-cals. From this it would follow, that the value, used for q_0 , is about 1.4 times too large, which would be a confirmation of the fact, that the mercury in the amalgam is not present as single atoms.

In order to obtain certainty as regards the molecular condition of the *tin* in the amalgam, it would be necessary to know the melting-point-line of the *mercury*, and to determine the lowering of the melting-point in addition to the heat of fusion in the presence of very small quantities of tin. There are indeed indications, that the tin is also not present as single atoms. Indeed, the quantity $r = -b_1 + b_2$,

which was found by us to be $-0,74$, gives for $\frac{b_2}{b_1}$ the value 0.26,

from which it would follow, that the molecular volume of tin (b_1) would be about four times larger than that of mercury (b_2). Now, the atomic volume of Hg is 14,7, that of Sn = 16,1, so if these two

components were monatomic, $\frac{b_2}{b_1}$ ought to be approximately = 1,

whilst in reality that relation is $\frac{1}{4}$; this points to the probability, that in the case of tin several (may be six) atoms are united to one molecule.

It certainly would be highly desirable if this question were fully investigated. For in all our calculations the values of x are only then valid, when both mercury and tin are assumed to be monatomic. This is also the case with all similar calculations, relating to other amalgams.

May I be allowed to point out, that the molecular condition of *mercury* may be determined from the lowering of the melting-point of *tin*, if this contains *a little dissolved mercury* — whilst the molecular condition of tin may be ascertained from the lowering of the melting-point of *mercury* in the presence of a *little tin*. For in the case of *dilute* solutions something is learned only about the condition of the *dissolved substance*, but never anything as regards that of the solvent. In the limiting formula

$$T_0 - T = \frac{RTT_0}{q_0} x,$$

where T_0 and q_0 relate to tin as solvent for example, everything on the right hand side will remain unchanged, although tin should not be monatomic, but say n -atomic. For x , the concentration of the dissolved mercury, would then become n -times greater, but q_0 would also become n -times greater, because the heat of fusion relates to 1 mol. = n -atoms. On the other hand, if the mercury were m -atomic, the value of x alone would change; x would then become m -times smaller, and we shall, therefore, observe a m -times smaller lowering of the melting-point than that, calculated on the basis of monatomicity.

In this way we might attain to the knowledge of the molecular condition at the ends of the curve, x being 0 (for mercury), and 1 (for tin). But in order to form further conclusions with other values of x , the whole of the meltingpoint-line would have to be accurately examined, and this may in many cases become an exceedingly complicated matter.

6. There is, however, another way to get to know something about the molecular condition of the solid tin, and that is the composition of the *solid* phase, which is in equilibrium with the liquid one. If we equate the molecular potentials of *mercury* in the two phases, we obtain:

$$e_2 - c_2 T + RT \log x + \frac{\alpha_2(1-x)^2}{(1+rx)^2} = e'_2 - c'_2 T + RT \log x' + \frac{\alpha'_2(1-x')^2}{(1+r'x')^2}.$$

This further gives:

$$(e_2 - e'_2) - (c_2 - c'_2) T = RT \log \frac{x}{x'} + \left[\frac{\alpha'_2(1-x')^2}{(1+r'x')^2} - \frac{\alpha_2(1-x)^2}{(1+rx)^2} \right],$$

or with $e_2 - e'_2 = q'_0$, and with introduction of the meltingpoint T'_0 of pure mercury:

$$q'_0 \left(1 - \frac{T}{T'_0} \right) = RT \log \frac{x}{x'} + \text{id.},$$

therefore

$$q'_0 = \frac{RTT'_0}{T - T'_0} \left[\log \frac{x}{x'} + \left\{ \frac{\alpha_2(1-x)^2}{RT(1+rx)^2} - \frac{\alpha'_2(1-x')^2}{RT(1+r'x')^2} \right\} \right].$$

Now in the liquid condition

$$\alpha_2 = \alpha_1 \times \frac{b_1}{b_2} = \alpha q_0 \times \frac{b_1}{b_2}, \text{ so } \frac{\alpha_2}{RT} = \frac{\alpha q_0}{RT_0} \frac{T_0}{T} \times \frac{b_1}{b_2} = \frac{\alpha}{\theta} \times \frac{T_0}{T} \times \frac{b_1}{b_2}.$$

This quantity is therefore $0,1144 \times \frac{504,8}{298,2} \times \frac{50}{13} = 0,745$.

Putting $\alpha'_2 = \alpha_2$ and $r' = r$ as a first approximation, the value of the correction becomes:

$$0,745 \left\{ \left(\frac{0,012}{1 - 0,74 \times 0,988} \right)^2 - \left(\frac{0,99}{1 - 0,74 \times 0,01} \right)^2 \right\},$$

and, as at 25° the composition of the liquid phase was found $x = 0,988$, and that of the solid phase $x' = 0,01$ (perhaps $0,06$), the said value becomes:

$$0,745 \times (0,0020 - 0,9950) = - 0,74.$$

A change of x' from $0,01$ to $0,06$ can only cause a slight alteration.

The value of the chief term $\log \frac{x}{x'}$ is:

$$\log^{10} \frac{0,988}{0,01} \times 2,3026 = 4,59,$$

so that we obtain (at 25°):

$$q'_0 = \frac{2 \times 298,2 \times 234,5}{63,7} \times 3,85 = 8450 \text{ gram-cals.},$$

whereas PERSON found $q' = 2,82 \times 200,3 = 565$ gr. cals. We therefore find a value 15 times too great. And a small error in the correction term $0,74$ cannot upset this result. If, however, the tin in the solid amalgam is taken as hexatomic, x' becomes six times greater and q'_0 comes down to about 4400 gram-cals. If, moreover, x' is originally taken not as $0,01$, but as $0,06$, so that with a hexa-atomicity x' now becomes $0,32$, the value q'_0 begins indeed to get more close to the value, obtained experimentally.

The above, therefore, contains indications enough of the polyatomicity of both mercury and tin. To arrive at a decision, however, accurate experiments will have to be made in the direction indicated, together with fresh determinations of the two heats of fusion.

Ethnology. — *“Influence of changed conditions of life on the physical and psychical development of the population of Central Borneo.”* By Dr. A. W. NIEUWENHUIS.

(Communicated in the meeting of February 28, 1903).

There is great diversity of opinion among competent authorities about the influence exerted by external circumstances of life on the development of a person and on that of the peculiarities of a tribe.

If this difference of opinion already gives evidence of the difficulty, of determining this influence for the individual, the difficulty is greatly

increased, as soon as we try to find, between two groups of men, characteristic differences, which are to be ascribed to their different circumstances of life. Examining the highly cultured nations which live in very complicated conditions of life, the difficulties become almost insuperable.

We are not a little hampered in this investigation by the fact that among civilized nations mutual intercourse and mixture have a disturbing influence on the eventual effect of special conditions of existence.

In Europe some data are furnished by the Israelites, which have preserved themselves as such for centuries in different countries under the circumstances prevailing there and which have absorbed few foreign elements. But here, too, the influencing conditions of life are very complicated, and the Israelites of the different countries have mixed with each other.

Chiefly because the relations in the societies of tribes, which have not reached so high a degree of civilization, are simpler and the conditions of life for all their members do not differ so much as elsewhere, it is likely that amongst them eventual changes in those conditions of life will stand out more prominently and that much becomes clear to the investigator, which was difficult to point out under more complicate relationships.

It is moreover noteworthy, that among them the influences of nature, of the surroundings in which they live, have a much greater effect than in higher civilized societies, which have learned to shield themselves better against this direct dependence.

We also meet with tribes where the great disturbing factor of frequent mutual intercourse and mixture is excluded in examining the modifications which two tribes have suffered by different external causes. A still simpler case presents itself where two large groups of the same race have lived for a long time under different external circumstances and have mixed little, if at all.

Before it has been proved that the people forming these tribes, are in their original qualities the same as Europeans, we must not directly apply what has been observed in them, to European society. For the right understanding of the pre-historic course of the development of mankind, however, we may refer to the tribes, which have reached as yet but a lower degree of culture; in my opinion we are equally justified in drawing certain conclusions as to the corresponding influences on higher cultured nations from many things, which we have observed in the social matters of the former.

During my second journey through Borneo I had the privilege of

living among two groups of the same tribe, which have existed for a century and longer under very different circumstances. They were the Bahaus on the Upper-Mahakam, with whom I lived for two years, and the Kénjas on the Upper-Kajan, with whom I spent some months.

The tribe-groups of this name occupy together the upper- and middle course of all the rivers, which fall into the sea on the North coast, beginning with the river Batang-Rédjang, and as far as the East coast, including the river Mahakam. They are called collectively the Pari-tribes, and they all consider the region containing the sources of the river Kajan as their original country. Mutual quarrels, the result of too dense a population, were the cause, that for centuries again and again tribes moved away to neighbouring rivers, as e.g. it happened no more than 25 years ago with the tribe Oema Timé, which settled on the Tawang, a tributary on the left of the Mahakam.

The Bahau-tribes on the Upper-Mahakam also originate from this native country, which they call Apo Kajan, but they have lived in their new home already for more than a hundred years. This was curiously confirmed on my arrival in Apo Kajan with my Bahau-escort. Their chieftain Kwing Irang then received for the first time a full account of the history of his ancestors, which was already forgotten in his own tribe.

How little intercourse the inhabitants of the Upper-Mahakam have with those of the Upper-Kajan may be derived from the fact that among all the younger Bahaus only one man had ever been in Apo Kajan, and that, when in the company of 60 Bahaus and 20 pseudo-Malays I set out on the expedition thither in August 1900 none of us knew the way. The journey lasted a month, and we had to traverse uninhabited land. The way was indicated by sticks put up in a special way in the river-mouths by some Kenjas who travelled in boats in front of us, the sticks denoting which rivers we had to take.

We may therefore assume as certain that we have to deal with tribes of the same origin, to which moreover their language, dress, morals and customs point, which distinguish them clearly from other tribes, e.g. from those on the Barito- and Lower-Batang Rédjang. Their descending from Apo Kajan to the Upper-Mahakam, however, brought the Bahaus in peculiar conditions, which exercised a great influence on them. On the Upper-Mahakam, namely, the Bahaus live at a height of from 250 to 200 metres, the Apo Kajan is 600 metres and higher. That this difference as regards the climate is very considerable especially in Borneo, may be derived from the

fact that in Java the region of moss vegetation does not begin lower than at a height of 2500 metres, whereas in Borneo it begins at a height of a thousand metres. This is caused by the following circumstances.

The situation of Borneo being under the equator, the middle region is but slightly affected by the influence of the trade-winds, which e. g. in Java make the difference between the wet- and the dry-monsoon so great. Hence it may happen that more rain falls from December to March than from May to October, but particularly in the highlands really dry times are unknown, and we may find low water in the rivers in the rainy period. The regular distribution of moisture through the whole year is greatly furthered by the circumstance that the whole island is covered with one large primitive forest, which itself retains large quantities of water, and harbours mouldering rocks which do the same. The annual rainfall amounting from 3000 to 5000 m.m. at different places, the climate is very humid all through the year, and the sky is always more or less overcast, so that a cloudless sky is a great rarity in the higher regions. Soon after sunset a low hanging curtain of clouds is formed in the valleys. This does not rise until seven o'clock in the morning or later and envelops the summits of the mountains till pretty late in the evening. In consequence of this the maximum temperature at a height of 250 metres is 30° C. in the shade on the Upper-Mahakam; at six o'clock in the morning however it was never lower than 20° C. Noteworthy is also that strong winds of long duration do not occur there, only some blasts of short duration, which are generally preceded by heavy showers.

The climate of Apo Kajan and of the Mahakam differs but little in most of its peculiarities, such as humidity, and a cloudy sky, but the latter is a good deal colder on account of the greater height, and what is particularly striking is the continually prevailing wind. This accounts for the fact that though in two months I never found a lower temperature than 17° C. at six o'clock a. m. and though it hailed but once, the climate is yet much rougher. The red cheeks, specially of the women and children prove this, and also the fact, that the different kinds of rice require a month longer to ripen in Apo Kajan than on the Mahakam. Yet the method of growing rice is the same, and consists in cutting down and drying the wood, after which it is burned and the rice sowed in holes, which are made by pushing pointed sticks into the soil, which is covered with ashes.

The geological formation is the same in Apo Kajan as on the Upper-Mahakam; we find in both a strongly denuded upland, where

everywhere old slate layers come to the surface. Only here and there younger formations, specially free-stone, cover the older.

If we now take into consideration that only in the last 30 years either the Bahaus on the Upper-Mahakam or the Kénjas on the Upper-Kajan have come into such close contact with higher civilized nations that it induced some of their men to undertake commercial enterprises for the purchasing of salt and linen, I think that I am justified in asserting that the two groups of tribes under consideration belong to the same race, that they have lived for upwards of a hundred years in countries with a different climate, that they have had but little mutual intercourse and have not mixed; that they have not changed their life as cultivators of the soil and have developed without external influences.

What effect this difference of climate can have on the population, may be derived from the fact, that in my opinion the thinness of the population in Borneo depends in the first place on the influences of the climate, and much more on the customs of the people than on the infectious diseases, such as cholera, smallpox, which are introduced from the coast. As both Upper-Kajan and Upper-Mahakam are so difficult to reach that infectious diseases but very seldom extend to them, we have, when trying to determine what the result of those changed conditions of life is for the Bahaus, only to deal with those factors which are sometimes comprised under the name of influences of the climate.

What is understood by influences of the climate in the highlands of Borneo became clear to me for the first time in the sultanate of Sambas on the West coast of the island, where I was struck by the difference in the spread of malaria among the population of the marshy coast regions and that of the highlands. In order to get a fuller knowledge of this difference, I made an inquiry into the traces of malaria infection on about 3000 children, both in the marshy alluvial plain and in the highlands. These children had not been offered to me on purpose for this investigation, but for an inquiry into the results of the vaccination among the Malay and Dajak population.

Among the population of the alluvial plains I found among 2103 children only 6 with a chronic hard splenic tumor, or 2,8 per 1000.

Among 420 children of the uplands it occurred in 403 children, or 959.5 per 1000.

The remaining 396 children originated from regions, which in their formation were the transition between the alluvial plains and the uplands. *Janus. Deuxième Année 1898.*

This inquiry yielded the result, that in the marshy alluvial plains which consist entirely of vegetable and animal remains, malaria hardly ever occurs, as opposed to the uplands where nearly all children suffer from chronic malaria-infection. At the same time I saw, that soon after birth the hardened and enlarged milt makes its appearance, for it was long before I could find a Dajak child of three weeks old, whose milt was not to be felt.

It is impossible to give the morbidity and the mortality caused by the malaria-infection among the population of the uplands in figures. I only found the death-rate in Sambas extending over 6 normal years, i. e. years without cholera or smallpox, to be for Dajaks 37 per 1000, for Malays 28 per 1000, which however does not represent the influence of the malaria, because there are also some Malays who live in the uplands and among those, who have chiefly settled in the lower plains, diseases of the digestive organs are much more frequent than among the hills.

In order to appreciate fully the influence of the malaria-infection on the existence of the inhabitants of the higher regions, we must dwell for a moment on the phenomenon, which prof. Koch says that he observed in New-Guinea, namely, that the native, who went through the malaria-process independently i. e. without any aid except his constitution, became immune against it. Many are the refutations adduced against this statement by physicians, who practised in New-Guinea. They all pointed out how frequently also adult Papocas suffered from malaria.

Judging by my experiences among the Dajaks, the truth lies between the two. I also have been struck by the fact that not so many hard enlarged milts as symptoms of the malaria-infection are met with among adult Dajaks as among children under the age of ten, which certainly points to a less strong influence of this infection. Moreover there is a great difference between the action of chinine on Dajaks and on Europeans, who are not immune. Though we must make allowances for other factors than immunity, yet it is remarkable, that we obtained much greater results with at most 1 gram sulphas chinini a day among the Dajaks than with 2 to 3 gr. murias chinini among European soldiers, seized by malaria in Lombok.

Among the former it was possible to cure not only the acute cases of malaria, but also cases which had continued from 4 to 6 months and had not been treated before, by administering 1 gram sulphas chinini per day and per dose during 8 days, whereas in the first four months after the war in Lombok in a mixed garrison of 1500 men more than 500 Europeans had to be removed, most of them by far

being malaria patients, whom I myself had treated with from 2 to 3 grams per day and per dose, and who had little chance of being cured in Lombok itself.

Among at the least 2000 Dajak malaria patients, whom I treated specially in Central-Borneo and of whom hardly any died, I observed another telling difference between the reaction of their body against the malaria-infection and that of the Europeans.

Whereas under unfavourable circumstances many of the latter perished under rabid and strong symptoms, sometimes so quickly, that chinine was of no avail, such acute cases with strong icterus, unconsciousness and collapse were never found among the Dajaks. I saw, however, many cases where the disease had reached an advanced stage after protracted illness.

That this difference was not due to the inferior strength of the infection in Borneo, was proved by my European and native fellow-travellers, most of whom suffered badly from malaria; to them I had again to administer from 2 to 3 grams of murias chinini a day, and one of them I had to give a strong hypodermic injection of 3,25 gram chinine within 36 hours.

From all this we may assume that the Dajaks become partially immune if in youth they are subjected to repeated attacks of malaria. Yet even then whatever weakens the constitution may give rise to attacks of malaria, so that diseases of the respiratory organs or of the digestive organs, wounds, diseases of infection and specially everything that is comprised under the name of catching cold, get complicated with malaria.

As the mountainous regions on the Upper-Mahakam are among those where malaria is of very frequent occurrence, it is clear, that the Bahau-population suffer greatly from it and that the individual experiences its enfeebling influence from early youth till death.

Being used for years in my practice among them to find that the great majority of cases were those of malaria, I was greatly struck by the change after my arrival among the Kënja population of Apo Kajan. I must add that my reputation as a physician procured me immediately after my arrival a great number of patients, though only few had ever seen a European on the coast before.

It first struck me, that so many hydropic old people called in my help, which had scarcely ever occurred in lower regions, whereas the malaria-cases retired to the background and during my stay confined themselves to a few acute cases. I found then, that the change in the sick-rate of the population was chiefly due to the prevalence of bronchitis with emphysema and heart-disease, bronchitis

being caused by the rough climate and increased by the smoking of badly prepared tobacco, which even very young children begin and which is held to be a remedy against coughing.

Though more acute malaria cases occurred, when the rough, cold weather set in with violent showers, there was not any question of a chronic infection of the population, manifesting itself in an enlarged, hardened milt in the children. This agrees with the well-known fact, that in a rougher colder climate malaria generally decreases in violence.

As bronchitis and its consequences do not make their enfeebling influence felt on the constitution before a more mature age is reached and are not to be compared in this respect with strong malaria-infection, I believe to have found the chief factor of the present difference of the two groups of the same tribe as to their constitution and their character in the difference of the occurrence of malaria as a consequence of the difference in height of the country of the Bahaus and that of the Kénjas.

Moreover I must take into account that syphilis is found in a less violent degree among the Kénjas than among the Bahaus. Among some Bahau tribes it was so universal, that I thought the fact that only tertiary forms were found could be explained by assuming exclusively hereditary transmission. Among the Kénjas, however, syphilis was also met with only in that form, but the cases were so isolated that we could not possibly ascribe them to hereditary influences. The cases observed seemed to have a less injurious influence on the general condition of the Kénjas than on that of the Bahaus. That this endemic form of syphilis is so much less common and that its symptoms are so much less dangerous among the Kénjas than among the Bahaus is due to a great extent to their stronger constitution.

If we now take into consideration, that among all these tribes every family, even that of the chiefs is dependent for its daily food and sustenance on the continual labour of all its members, which is not the case in more highly civilized societies, we feel, how great the influence must be which the more or less frequent occurrence of these diseases must have on the prosperity of the tribe.

A striking example of the better conditions of existence offered by Apo Kajan which is of equal extent to the Upper-Mahakam, compared with the lower river-basins, is furnished by the fact that for centuries many tribes have been leaving this country for other parts of the world and that nevertheless the population there is at present much denser than in other Dajak regions.

Instead of 300 to 800 inhabitants as on the Upper-Mahakam, the villages count there 1500—2500 inhabitants, though they certainly do not lie farther apart. Moreover the general appearance of the Kēnjas makes a much better impression because of their stronger build and the less frequent occurrence of deforming diseases among the scantily dressed figures, which is enhanced by the absence of the cachectic persons so numerous elsewhere.

The difference between the Bahaus and the Kēnjas is even more marked in their psychical qualities than in their physical individuality. The enfeebling moments which on the Mahakam affect them in a so much larger degree seem to have had a strong degenerating effect on the psyche of the Bahaus.

This is proved by their history: in the beginning of the 19th century they made themselves known not only by head hunting but also by raids undertaken on a larger scale till far into the river-basin of the Kapoewas, the Barito and the Mahakam, in which regions no tribe could resist them; at present smaller forays rarely occur, larger expeditions are quite out of the question and in a fight with other tribes the wounding or death of one man may put his tribe to flight.

The greatest difficulties which confronted the European stranger in his intercourse with the Bahaus, arose in his continual struggle with their timidity, fear and suspicion even after a long intercourse and in the fact that his movements were continually hampered by the peculiar religious and other convictions of these tribes. The strong contrast in these respects between them and the Kēnjas is therefore very striking.

After my arrival in Apo Kajan I was at once struck by the fact, that the 150 men, who had come under their principal chieftain to assist me by bringing boats and improving roads, were much freer and noisier in their behaviour than my Bahau escort, that the chieftains gave their commands with much greater energy and that they were also better obeyed. During my stay in their villages this impression was greatly strengthened by the want of shyness on the part of the women and children. Remarkable was the contrast between the behaviour of the young Kēnjas and the Bahaus when I, as I usually did, distributed small presents, such as beads, finger-rings, needles and pieces of cloth among them. Among the Bahaus I could quietly keep in my chair, and though occasionally a little hand may have been stretched out too quickly towards the coveted object, yet all the little ones waited patiently for their turn and never became boisterous. When I distributed things among the Bahaus, the proceedings were quite different: I had to begin with taking a

firm footing, for boys and girls pressed in upon me with loud shouts and extended hands; every one was afraid to be behind hand and they scuffled among each other, to get nearer. It soon proved that they are less sensible to the bad smells of their fellow-men than the Bahaus among whom one can sit for hours with impunity even in large companies; therefore they also prefer to go a long way round rather than pass a dead body, and who protest to a disagreeable smell by violent gestures and spitting.

Remarkable also is the greater perseverance of the Kënjas at labour, which I specially observed when making long expeditions in rowing-boats on the Mahakam in the great heat to which they were not used. Though they are more used to walking than to rowing in their highlands, where the roads are better and the rivers smaller than in the country of the Bahaus, yet they kept on rowing for days together much more persistently than the latter, and always arrived earlier.

These few examples already give evidence of a greater vivacity, less sensibility and also of a greater power of resistance of the nervous system; moreover their mental capacities are far superior.

When telling the Bahaus about some remarkable features of our society, I got accustomed to meet with an absolute incapacity to imagine these things, which gave rise to disbelief, and induced them, but often after a long interval, to try and catch me at an untruth. Among the Kënjas, however, I soon concluded from their questions, that they at least tried to imagine railroads and similar inventions, and that they really understood other things. A very good criterion is furnished by the explanation of the motion of the sun, the earth and the stars with the origin of night and day, and the causes of a solar- and lunar eclipse. Of course the Kënjas also did not immediately believe that the earth is round and moves, nor that it is not a monster that eats sun and moon in case of an eclipse, but they understood at least my explanation.

Of practical use to us was the greater interest and the more extensive knowledge of their surroundings shown by the Kënjas.

In the course of our topographical survey of the Mahakam and when inquiring into the names of the principal mountains and rivers we met among the Bahaus with such utter ignorance, that we were for a long time convinced they were unwilling to tell them to us. It proved however later on, that it was not unwillingness on their part, but that only few among them knew anything about rivers and mountains outside their immediate neighbourhood, and that e.g. high mountains, which, though they stood at some distance on the territory

of another tribe, but commanded the landscape, had no name among them, and that in order to find out its name, we had to apply to tribes living nearer the mountain. It was, of course, quite out of the question to avail ourselves of their help in determining the different places from such a mountain top.

I was therefore greatly struck, when among the Kénjas I ascended a mountain, for the purpose of getting a survey of their country and Boei Djalong, the chief of the country, who accompanied me pointed out all the mountains as far as the horizon with their names, also those we could verify in the Mahakam territory; he also indicated the roads leading to the different adjoining countries as accurately as a European could have done.

Not only we, but also the Bahaus who accompanied me, were astonished at the knowledge of the history of times long past, which the Kénjas displayed. It is a wellknown fact that tribes, who cannot write and who possess a low degree of civilization, lose quickly the memory of past events, and the knowledge of the Bahaus about their ancestors was therefore very inaccurate. Great was therefore the astonishment of Kwing Irang, when the Kénjas told him the traditions of his own ancestors during the time of their stay in Apo Kajan.

This greater development of their psyche keeps pace with phenomena, which evidence a stronger personality as regards their surroundings. They are braver, which appears clearly from their way of conducting warfare. The tribes in Borneo are notorious on account of their headhunting, a method of taking revenge and of fighting, which is justly looked upon as being rather cunning and cowardly than brave, as it consists in the laying of ambushes and the sudden attack of superior forces on but a few individuals. An open fight is rare among the Bahaus, and as has been said before, if two tribes are confronted, the death or wounding of one man suffices to put his party to flight. Quite different is the warfare among the Kénjas: hand-to-hand fights are frequent, in which chiefly the sword is used, and in which many are killed before the battle is decided. Though headhunting occurs also among them, yet it recedes more into the background, and when it occurs more personal valour is displayed. A few years ago e. g. a young Kénja chieftain, when performing a war-dance during a visit on the Mahakam, suddenly cut off the head of one of the spectators, and took it with him in his flight. This was certainly treacherous, but it requires courage to do such a thing in a large gallery with a great many lookers-on.

It is irritating to see, how the Bahaus submit to be illtreated by the Malays, who live at their expense by deceit, theft and grave-

robbery etc. Only rarely do they take revenge on these unwelcome guests, who live among them either because they gather the forest products, or because they had to fly from the coasts on account of crimes.

The Kënja-tribes are less long-suffering: two gangs of Malays, one consisting of five members from the Mahakam and one of eight from Sërawak, who tried to live upon them in a similar way, were all murdered.

As soon as we come in contact with the Kënjas, this bold personality impresses us favourably. Among the Bahaus we could not establish for years the frankness of intercourse between them and ourselves, which was brought about with the Kënjas in as many months. Only incidentally and by indirect means could I get to know among the Bahaus what they thought of a plan and what they intended to do. When alone with one of them I occasionally succeeded in getting him to express his thoughts freely, because he had no reason to be afraid of his fellow tribes-men, but they never quite relinquished their fear and distrust.

In our intercourse with the Kënjas the last trace of suspicion had soon vanished, and never shall I forget the impression made by their political meetings on us Europeans, used to the uncertain, hesitating and insincere behaviour of the Bahaus, even when discussing affairs of great importance. In the meeting of the Kënjas all the chiefs present freely expressed their opinions with peculiar ceremonies on subjects as e. g. whether it was advisable to adhere to the rajah of Sërawak or to the Dutch-Indian government, and the advantages and disadvantages were openly discussed.

If on account of these peculiar qualities the behaviour of the Kënjas is noisier, coarser, braver and less sensitive than that of the Bahaus, it is interesting to see what influence this has had on their society. Among the Bahaus on the Mahakam we find a number of perfectly unconnected tribes, in which every individual considers himself quite independent of all the others, and perfectly free to look upon his own interest as of chief importance, which renders the chiefs powerless to exert any influence over their subjects for more general interests and enterprises. Everybody entertains the greatest fear for unexpected sudden attacks from far or near, and while in the day-time the men always go to their rice-fields strongly armed, in the evening they dare not even be under their houses without a naked sword. Of course women and children are still more afraid.

Among the Kënjas, on the contrary, we find a somewhat loosely constructed, but yet connected whole of all the tribes under the

acknowledged supremacy of the tribe of the Oemo Tow and its chief Boei Djalong. The country is so safe, that the population goes to the fields only armed with a light spear as support, and that women unarmed and unaccompanied dared to come and visit me from neighbouring settlements at many hours' distance through the primitive forest or in boats.

In this better regulated society the higher moral qualities of the Kēnjas also stood out to advantage. If among the Bahaus the want of interest in the public welfare was strongly felt, among the Kēnjas this was different. In the character of the Kēnja chiefs a sense of responsibility and disinterestedness came to the front accompanied with more moral courage and influence on their subjects. When questions arose as to wages, the payment of which always consisted in goods chosen by the party concerned, the Bahau chiefs always retired for fear of quarrels with their people. Among the Kēnjas the chiefs calculated, how much was due to each of their people, took it home and distributed it there.

When it had been resolved in the political meetings, that representatives of several tribes should go with me to the Mahakam, hundreds of Kēnjas prepared to go. Bad omens for the journey, however, caused more than 400 to draw back, and though the principal chiefs might have done so too, they only sent back their followers and went on themselves, because they felt the great importance of carrying on the negotiations.

Among the Bahaus no chief would easily have gone to look after the general interests, and certainly not against bad omens.

Also the conduct of their inferiors during the journey was quite different. Eighty Kēnjas succeeded in deriving the required favourable omens from the flight of birds, the cries of does and the appearance of certain snakes, and accompanied us. Though from different villages, they formed one company, having their victuals in common, and when the Bahaus and ourselves had not enough they shared their stock with us, which was then soon exhausted. They had, however, full confidence in my assurance that I would buy them fresh provisions on the Mahakam.

The different groups in a Bahau escort never voluntarily share their rice with each other, and when I and my Malays were in want of rice on the journey, we could only get some from them at very high prices. At last a young man had the assurance to ask me three times that exorbitant price for his rice, though as a physician I had saved his life, and had treated all of them without asking any reward.

In spite of the great advantages, which the Bahaus derived from our stay, I never met with any direct proofs of gratitude; they only put somewhat greater confidence in me than in other strangers. When however I left a Kënja tribe after a six days' stay, the family of the chief came personally to thank me for everything I had given to them either by way of exchange, presents or medicine; the first expression of gratitude for many years.

All this proves that the Kënjas of Apo Kajan are far superior to the Bahaus also as regards those traits of character, which are considered as higher ones among Europeans.

Another striking example of their stronger personality is furnished by the way, in which their religious ideas influence their existence.

From their standpoint as agricultural tribes of fairly low development, with whom the influence of nature on their principal means of subsistence, agriculture, and on their persons in diseases and disasters is strongly felt, these peoples contemplate their surroundings with great fear. Their thoughts about these surroundings and the place they occupy in them, which represent their religious conviction, are not of a very elevated nature.

They think that their lives are ruled by one chief god, whom they call Tamei Tingei, our high father, and who punishes already on earth all crimes with adversity, disaster, disease and death. For the execution of his will he makes use of a host of evil spirits, who people all nature around.

All calamities and diseases, therefore, even death on the battlefield or at a confinement, are to these tribes the manifestations of anger of their chief god with regard to the sufferer, who has incurred this anger by the conscious or unconscious violation of human usages or divine laws.

When the attempts, to guard themselves against the manifestations of the anger of their god by observing these laws and usages scrupulously, proved fruitless, they tried to reach their aim by extending the prescribed laws to the minutest details, so that they have definite precepts as to the course to be followed not only in all emergencies of every day life, but also in agriculture, the chase and fishery.

All these precepts are called pëmali, and they render certain actions in certain cases lali, pantang or taboe.

If the observation of the pëmali is to shield them from the evil spirits, they enjoy the assistance of a whole multitude of good spirits, indirectly through the mediation of the priests and priestesses or directly by warning omens, which are communicated by certain birds, snakes and does, and also by certain events. These omens are very numerous, and are strictly followed, especially by the Bahaus.

As however these pēmalī and omens have risen, independent of the true requirements of the existence of these tribes, they have constantly a disturbing influence. To give an example: the Bahaus, when growing rice, do not regulate their work according to dry or wet weather, or to the condition of their fields, but all the families of a tribe have to conform to what the chieftain does, and he sees that the necessary religious rites before the special successive agricultural proceedings are duly performed. When the preliminary rites for the sowing have commenced, no one is any longer allowed to burn dead wood on his field; if the chief is weeding, every one must cease his sowing, etc.

In the same way they begin all important enterprises, such as travelling, the building of a house, etc. not according to the demands of the moment, but according to whether a bird flies up to the right or to the left, and whether a doe is heard or not.

Of course, stronger races do not so meekly submit to the galling restraints of these pēmalī and omens, as more timid natures. I had an opportunity of observing this as a characteristic difference between Bahaus and Kēnjas. It is true that both have the same religion and that their pēmalī and omens are essentially the same, but the pēmalī are more developed among the Bahaus and go more into details, than among the Kēnjas. Among the former all the adults in a tribe are obliged to observe the pēmalī closely; among the Kēnjas the priests are specially charged with this, so that the mass of the people have more liberty.

Among the Bahaus e.g. nobody eats the flesh of the stag; among the Kēnjas the priests only do not take it.

The Kēnjas have not introduced the above-mentioned very injurious precepts for the growth of rice with the same restrictions. It is true that also among them the chief causes the necessary ceremonies to be performed, but still, every one is free afterwards to do in his field, what will prove necessary, and this is of the greatest importance for the success of the harvest.

The Bahaus cling much more scrupulously to the existing pēmalī and omens than the Kēnjas. In spite of my having lived for years among the Bahaus, I was forced, to observe their precepts as scrupulously as they themselves did. Only in case of urgent necessity I dared set out on a journey or receive a patient during the time prohibited by their laws, and I was therefore as much shut out from the outer world as they were. Once they made the inhabitants of their own village on their return from an eight months' expedition remain in the forest, starving, rather than violate the lālī of their village by admitting them or bringing them provisions.

When I arrived with my companions among the Kënjas, the principal chief and his family happened to be in the condition of lali, but in order to be able to receive us he quickly had a new house built in another place for the priest family in his house, who were the principal bearers of the pëmali. By this means it was permissible for him to receive us in his house.

Later on we proceeded to another village, where the house of the principal chieftain was also lali. For our reception he divided his house, which was very long, into two parts by means of a gate, so that we strangers could not enter the one part. In the other he received us.

The Kënjas watch the omens before every enterprise as earnestly as the Bahaus, but as soon as they are in conflict with the requirements of the moment, they dare take their own course to a much greater extent.

I have already mentioned that the Kënja chiefs ventured to accompany me to the Mahakam in spite of the bad omens of their birds.

In case of imminent danger, e. g. if an enemy is thought to be hidden in the neighbourhood, the Kënjas disregard omens.

So we see among the Bahaus the more scrupulous observance of a more developed system of religious usages keep pace with the deterioration of many of their physical and psychical qualities. In these the Bahau is inferior to the Kënja, which can originally not have been the case, but which is owing to the change of abode of the Bahaus more than a hundred years ago, because through this change they were exposed to the more injurious influences of their new surroundings, the principal of which is a greater prevalence of malaria.

Mathematics. — Prof. P. H. SCHOUTE discusses: “*Relations between diagonals of parallelotopes*” with a view to show by a simple example how it is possible that investigations of more-dimensional figures lead to new theorems on figures of our three-dimensional space. This example relates, as the title indicates, to those figures which continue in the spaces with more than three dimensions the well-known series of line-segment, parallelogram, parallelepipedon . . . and can therefore be called by the name of parallelotopes. Here diagonal always denotes a line connecting — across the inner part of the enclosed space — two opposite vertices. *First* our attention may be drawn to the fact that the number of diagonals of the parallelotope is doubled

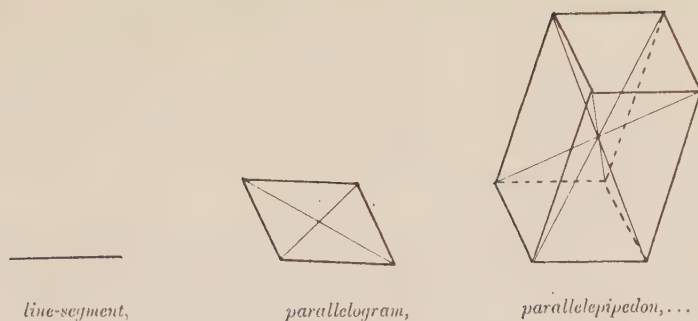


Fig. 1.

every time a new dimension is added, whilst the number of constants determining the figure, though at first larger than the number of diagonals, increases less strongly than the latter; this is illustrated by the following little table, where under each other the corresponding values of the number n of the dimensions, the number d of the diagonals and the number g of the determining constants are indicated, whilst the meaning of h is explained further on.

n	2	3	4	5	6	7	8	9	10	...	n
d	2	4	8	16	32	64	128	256	512	...	2^{n-1}
g	3	6	10	15	21	28	36	45	55	...	$\frac{1}{2} n(n+1)$
h			1	5	16	42	99	219	466	...	$2^{n-1} - \frac{1}{2} n(n-1) - 1$

From this is evident in the *second place* that when constructing parallelogram and parallelepipedon all diagonals can be used as determining lines, but that this is not possible for the parallelotope P_5 with five and for the following parallelotopes $P_6, P_7 \dots$ with still more dimensions; and from this ensues in the *third place*, what becomes the principal thing here, that between the 16 diagonals of P_5 at least *one* relation must exist and that this number of relations for $P_6, P_7 \dots$ must increase consecutively to 32—21 or 11, 64—28 or 36, ... If in the *fourth place* we wish to trace those relations and try to do so under the condition that the length of all the edges must figure amongst the determining data, then we find that the sum of the squares of all the diagonals — always equal to the sum of the squares of all the edges — is known at the same time, and that the other relations, between the diagonals only, always present themselves in the form of homogeneous equations, the number h of which is indicated above. This includes that already for the parallelotope P_4 we come across a relation between the diagonals. This simple relation can be expressed as follows: If we divide (Fig. 2) the eight vertices of one of the eight parallelepipeda forming the boundary of

the four-dimensional figure into two groups (A_1, A_2, A_3, A_4) and (B_1, B_2, B_3, B_4) of non-adjacent vertices, the sum of the squares of the diagonals terminating in the four points A is equal to the sum of the squares of the four remaining ones, terminating in the points B . And from this ensues, the common centre of the eight diagonals being indicated by O , the equation

$$OA_1^2 + OA_2^2 + OA_3^2 + OA_4^2 = OB_1^2 + OB_2^2 + OB_3^2 + OB_4^2,$$

or in words: If we divide the eight angular points of a parallelepipedon into two groups of four non-adjacent points, the sum of the squares of the distances from an arbitrary point O to the points of each of

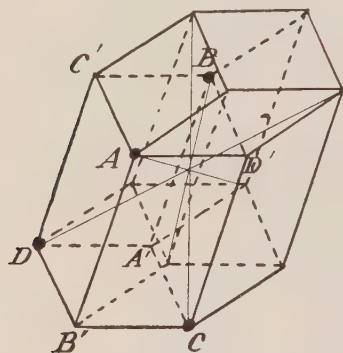


Fig. 2.

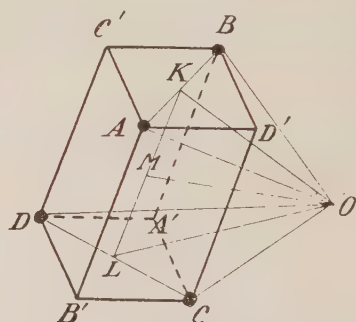


Fig. 3.

the two quadruples is the same. If we now suppose in the *fifth* place that this point O lies with the parallelepipedon in the same three-dimensional space, our space I may say, we finally find the following theorem belonging to our solid geometry:

"If we connect (Fig. 3) an arbitrary point O of space with the two quadruples of non-adjacent vertices of a parallelepipedon, we obtain two quadruples of line-segments for which the sum of the squares has the same value."

This simple theorem which up till now I never came across in any handbook is of course easily proved; we have but to know the formula for the median line in a triangle. With the help of this formula we find that, disregarding quantities not depending on the place of O , the sum of OA_1^2 and OA_2^2 can be replaced by two times $OC_{1,2}^2$, the sum of OA_3^2 and OA_4^2 by two times $OC_{3,4}^2$, and twice the sum of $OC_{1,2}^2$ and $OC_{3,4}^2$ by four times OM^2 ; from which is evident that for the two sums named in the theorem, disregarding the *same* quantities not depending on O , the same value is found, namely four times OM^2 , etc.

Finally this observation: it is not our purpose to emphasize even in the slightest degree the above-mentioned theorem, up till now accidentally remained unnoticed. Neither have we in view to point out that for each parallelotope P_n the diagonals and the sides furnish equal sums of squares and that all possible relations between diagonals mutually can be represented in the above mentioned form. Whilst referring for this to a paper, to appear shortly in the "Archives Teyler", we repeat here, that this short communication was given to satisfy the wish to show also to non-professional mathematicians by means of a simple example how the study of polydimensional geometry may lead i. a. to the discovery of new theorems of plane or solid geometry.

Chemistry. — "*On the atomic weight of Antimony.*" By Prof. ERNST COHEN and Mr. TH. STRENGERS. (Communicated by Prof. W. H. JULIUS).

(Communicated in the meeting of February 28, 1903.)

1. In connection with a physico-chemical study on the nature of so-called *explosive antimony* conducted by one of us (C.) conjointly with Dr. W. E. RINGER, the question of the exact atomic weight of antimony became a very important one.

Notwithstanding a number of investigators¹⁾ have attempted to determine this atomic weight, it is not as yet known with sufficient certainty.

CLARKE²⁾ sums up his criticism on the determinations made up to the present with these words: "... This result, therefore, should be adopted until new determinations of a more conclusive nature, have been made."

¹⁾ BERZELIUS, POGGEND. Annalen **8**, 1 (1826); KESSLER, *ibid.* **95**, 215 (1855); SCHNEIDER, *ibid.* **98**, 293 (1856); ROSE und WEBER, **98**, 455 (1856); DEXTER, *ibid.* **100**, 363 (1857); DUMAS, Annales de chimie et de physique (3), **55**, 175 (1859); KESSLER, Pogg. Ann. **113**, 145 (1861); UNGER, Archiv der Pharmacie **197**, 194 (1871); COOKE, Proc. Amer. Acad. **5**, 13 (1877); KESSLER, Ber. deutsche chem. Gesellschaft, **12**, 1044 (1879); SCHNEIDER, Ueber das Atomgewicht des Antimons, Berlin 1880. Journal f. prakt. Chemie (2) **22**, 131 (1880); COOKE, Amer. Journ. Sciences and Arts, May 1880; B. B. **13**, 951 (1880); PFEIFER, Lieb. Ann. **209**, 161 (1881); POPPER, *ibid.* **233**, 153 (1886); BONGARTZ, B. B. **16**, 1942 (1883); G. CL. Friend and EDGAR F. SMITH, Journal Americ. Chemical Soc. **23**, 502 (1901).

²⁾ The constants of nature, Smithsonian Miscellaneous Collections Part V, Washington 1897.

2. POPPER¹⁾, under VON PEBALS guidance has tried to make a determination of the atomic weight by an electrical method.

He connected in the same circuit a silver coulometer and a cell containing a hydrochloric acid solution of antimony trichloride. A rod of pure antimony (wrapped in linen) suspended in the liquid constituted the positive electrode, whilst the negative electrode consisted of a weighed platinum wire.

During the electrolysis the electrolyte was kept in continual motion by means of a stirrer so as to exclude local changes in the concentration of the liquid.

Under these circumstances explosive antimony is deposited on the negative electrode²⁾. POPPER fused the substance formed in a tube made of hard glass in an atmosphere of nitrogen; in this way the antimony trichloride present in the metallic mass was expelled. As soon as all the chloride had volatilized the antimony regulus was washed first with solution of tartaric acid, then with water, dried at 120° and weighed. Additional experiments had proved that the glass tube did not suffer any alteration in weight on heating and melting the metal contained therein.

The silver electrode in the coulometer was wrapped in a piece of linen. After the electrolysis was completed, the silver which had deposited in the platinum dishes employed was boiled and washed with water until this no longer gave a reaction with hydrochloric acid and it was then dried at 120°.

POPPER's results obtained in the electrolysis of solutions containing respectively 7 and 22 per cent of SbCl_3 are given in the subjoined table. We have, however, recalculated the data as POPPER still uses the atomic weight 107.66 for silver whereas more accurate investigations have shown this to be 107.93.

In a second series of experiments in which a few more improvements had been made as regards the insulation of the silver coulometer, POPPER found for 7 per cent solutions as equivalent weight the value 40.33, therefore as atomic weight the value 120.99.

As he could not discover any sources of error in his process and still believed in the accuracy of the results obtained by COOKE, who, by purely chemical means, had found the atomic weight of antimony to be 119.9 he concludes his paper with the words: "Sollte nicht die Entdeckung des Elements "Germanium" durch WINKLER den

1) Compare 1.

2) Such was the case with solutions containing 22 per cent of SbCl_3 . In solutions containing 7 per cent. POPPER obtained crystalline *non*-explosive antimony. I will fully refer to this particularity later on in my paper with Dr. RINGER. (COHEN.)

Grams of Sb Cl ₃ in 100 Grams solution.	Weight of the metal deposited in the same time circuit in the same time.		Electrolytic equivalent	Atomic weight.
	Antimony	Silver		
			of Antimony (Silver = 107.93)	
7	1.4788	3.9655	40.25	120.75
7	2.0074	5.3649	40.39	121.17
7	4.1893	11.1847	40.43	121.29
7	4.1885	11.1847	40.42	121.26
7	5.6869	15.1786	40.43	121.29
7	5.6991	15.1786	40.46	121.38
22	1.4856	3.9655	40.43	121.29
22	2.0120	5.3649	40.47	121.41
22	3.8882	10.3740	40.45	121.35
22	3.8903	10.3740	40.47	121.41
22	4.2710	11.3868	40.48	121.44
22	4.2752	11.3868	40.52	121.56

Weg andeuten, auf welchem die Lösung des vorliegenden Rätsels zu suchen sei?"

3. We have not only repeated the research of POPPER but also extended the same by using hydrochloric acid solutions of SbCl₃, whose concentration varied between 2.3 and 83.3 percents of SbCl₃ by weight.

It was necessary to pay particular attention to the purity of the materials employed. The antimony trichloride was obtained from MERCK; 20 grams were dissolved in solution of pure tartaric acid and then digested on the waterbath for some hours with excess of clear sodium sulphide. The liquid remained perfectly clear¹⁾.

Some kilos of this antimony chloride were precipitated with sodium carbonate free from foreign metals, the precipitated Sb₂O₃ was washed, dried and reduced to metal by fusion with pure potassium cyanide in a PERROT's furnace. The crucibles used were previously tested to see whether they would yield any foreign metal to potassium cyanide but we could not prove the presence of any impurity in the melt.

¹⁾ As commercial antimony generally contains lead whose atomic weight exceeds that of antimony it was absolutely necessary to prevent the possibility of any lead being present in the materials employed.

The fused metallic antimony was poured into cylinders of asbestos paper tied round with copper wire: the rods of antimony thus formed were cleansed with hydrochloric acid and washed.

By way of control we dissolved a piece weighing 20 grams in pure strong nitric acid with addition of 75 grams of crystals of tartaric acid. The clear acid solution so obtained was rendered alkaline by adding small lumps of sodium hydroxide prepared from metallic sodium (the lye was free from foreign metals) and digested on the waterbath with a clear solution of sodium sulphide but gave no precipitate.

The solutions were prepared by weighing the pure antimony trichloride roughly and dissolving the same in pure hydrochloric acid of 1.12 sp. gr. at 15°. The exact composition of the solutions was determined by electrolysis of the liquid in presence of sodium sulphide according to NEUMANN's directions ¹⁾.

4. In each experiment two silver coulometers were put into the circuit; one in front and one behind the series of antimony solutions which took part in the electrolysis. The coulometers consisted of 200 cc. platinum dishes with rough inner surfaces. We will not omit to point out that such dishes are particularly suited for coulometric determinations as it is possible to precipitate in them a large amount of silver with little chance of any traces being detached on washing the precipitates ²⁾. The amount of silver deposited in our experiments varied from 25 to 50 grams whilst when using the smooth dishes usually employed it is difficult to handle a few grams without loss.

As electrolyte we used a 10 or 15 per cent neutral solution of silver nitrate; no difference was noticed with these solutions. The positive silver plates were cast of silver which we received from Dr. HOITSEMA, Comptroller-general at the local Government Mint. On analysis, we could not trace foreign metals in 100 grams of this silver. The plates were 6.5 c.m. in diameter and 4 mm. thick. They were surrounded by a covering of filter paper (SCHLEICHER and SCHULL). Each silver plate was suspended by a thick platinum wire. The coulometer dishes after being filled with the silver solution were covered with a glass plate with a hole in the centre through which a platinum wire was introduced.

¹⁾ Analytical Electrolysis of Metals, Halle 1897. S. 145.

Here, we provisionally took the atomic weight of antimony to be 120; as will be seen from what follows, the uncertainty of the atomic weight is of no consequence *here*.

²⁾ Compare KAHLE. WIED. Ann. 67, N.F. 1 (1899); RICHARDS, COLLINS and HEIMROD, Proc. American Acad. of Arts and Sciences XXXV, 123 (1899). RICHARDS and HEIMROD, Zeitschr. f. physikalische Chemie 41, 302 (1902).

Great care was bestowed on the insulation of all the apparatus. The conducting wires were strongly insulated and were, as far as possible, in contact with air only. Each platinum dish was placed on a copper plate which stood on a glass plate; the latter was carried by porcelain insulators which acted as feet.

For a rough orientation a technical ammeter was included in the circuit; the current was taken from 1 to 3 storage cells.

5. The antimony solutions which were subjected to electrolysis were contained in spacious beakers (1 litre) (*B* in fig. 1) in which constant stirring could take place by means of WITT's centrifugal stirrers. A HEINRICI hot-air motor kept all the stirrers in motion. The rods of antimony which served as positive electrodes were surrounded by a piece of linen which was fixed to the rod with platinum wire, or by glass tubes closed at the lower end containing a large number of not too small perforations (*O, O, O . . .*) (3 or 4 m.m.). The object of surrounding the rods was to prevent any loose particles of antimony from getting into the liquid.

As negative electrodes we used platinum wires (*P*) about 10 cm. in length and 0.3—0.4 mm. thick; they were provided at the upper end with the capillar glass pieces (*C*), on which a number was engraved.

Both antimony rods and platinum wires were attached to copper binding screws which moved along glass standards (*S*). In order to prevent contamination of the liquids by contact with copper, a piece of platinum wire (*Pt*) was placed between the binding screws and the rods of antimony or platinum suspended thereby.

6. The experiments were now conducted as follows: After the platinum wires had been weighed they were put in their places; the silver coulometers were connected up and the current closed. At the commencement the strength of the current may only amount to a few hundredths of an ampère; if this is exceeded, evolution of hydrogen instead of separation of antimony takes place. When the precipitate on the platinum wires had reached a certain quantity, when in other words, the surface had become enlarged the strength of the current was increased and gradually raised to about 0.3 ampère.

At the end of the electrolyses the rods were rinsed with a 12 per cent solution of tartaric acid ¹⁾, then washed with water, alcohol and ether and dried over sulphuric acid in a desiccator.

¹⁾ By a special experiment we had convinced ourselves that this did not cause any perceptible diminution in weight.

To determine the amount of antimony separated by the current the following method was adopted ¹⁾.

The rod was placed in a tube of hard Jena glass closed at one end (length of the tube 30 cm., diameter 1 cm.). This tube had been previously cleaned, strongly heated in a current of dry air (dried over H_2SO_4 and P_2O_5) and then weighed. The antimony rod was now weighed and by way of control the tube and rod were again weighed together.

The air from the tube was now expelled by means of a continual stream of carbon dioxide which had been dried over sulphuric acid and phosphoric anhydride. The tube (*explosion-tube*) was then closed with a properly fitting india-rubber cork and put into a metal cooling vessel made of composition tube in the manner represented in fig. 2. This tube was connected with the water tap.

If now the explosion tube is shaken for a moment the explosive antimony explodes. The tube is then strongly heated with a triple burner on the spot containing the rod; the SbCl_3 evolved condenses on the cold wall of the tube to a clear white mass. The heating is continued until the antimony is perfectly fused and this is then allowed to cool slowly. The tube is then opened, the SbCl_3 is removed by rinsing with a mixture of alcohol and ether (3:1) the tube is then rinsed with ether and dried by heating in a current of dry air as described above.

The tube with the antimony regulus is now weighed.

A previous experiment had proved that the explosion tube suffers no alteration in weight by the heating and subsequent treatment. It was found for instance that an explosion tube weighed 29.6614 gram before the experiment and 29.6610 gram after the experiment the contents having been removed by means of nitric and tartaric acids.

By way of illustration one of the experiments is reproduced in detail whilst the results of the other measurements are united in a table.

Electrolysis of a 15.6 proc. SbCl_3 solution.

Silver coulometer N^o. 1.

weight of platinum dish + silver				73.1920	grams
"	"	"	"	36.7310	"
weight of silver				36.4610	grams

¹⁾ Further particulars about this method will be found in the paper of COHEN and Dr. RINGER.

Silver coulometer N°. 2.

weight of platinum dish + silver 71.4530 grams

"	"	"	34.9902	"
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weight of silver 36.4628 grams

weight of explosiontube + regulus + platinum wire 55.0281 grams

"	"	"	41.0780	"
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weight of regulus + platinum wire 13.9501 grams

weight of platinum wire	0.2696	"
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weight of regulus 13.6805 grams

From this result the equivalent weight of the antimony is calculated as follows:

$$\frac{107.93}{36.4628} \times 13.6805 = \mathbf{40.49}.$$

The results so obtained are collected in the following table. (p. 550).

From this table we see that the atomic weight obtained increases with the concentration of the SbCl_3 solutions and varies between 120.87 and 121.89 within the concentrations 2.3 and 83.3 per cent.

From this it is quite plain that we cannot arrive at the determination of the atomic weight of antimony by the electrolysis of solutions of antimony trichloride and that the values found by POPPER, to which in the calculation of the atomic weight is attached the same value as to those of SCHNEIDER, COOKE and BONGARTZ¹⁾, are quite accidental, being dependent on the concentration of the solutions employed.

It further appears from the above that unknown electrolytic or chemical changes play a part here which require further investigation and which may be expected to add to our knowledge of the formation and composition of the remarkable explosive antimony.

We hope, shortly, to investigate these changes.

¹⁾ Compare OSTWALD. Lehrbuch der allgemeinen Chemie I, 53 (1891).

Grams of Sb Cl ₃ in 100 grams solution.	Weight of the antimony regulus in grams.	Weight of the silver in the Coulometer in grams.		Equivalent weight of the Antimony.	Atomic weight of the Antimony.
		Nº. 1.	Nº. 2.		
2.3	16.8747	45.2069	45.2019	40.28	120.87
2.3	14.5914	39.6805	39.0816	40.29	
3.4	18.7961	50.3791	50.3860	40.26	120.78 ¹⁾
5.0	16.9175	45.2019	45.2069	40.38	121.17
5.0	14.6298	39.0805	39.0816	40.39	
5.3	18.8627	50.3791	50.3860	40.40	121.20
5.3	12.6206	33.7224	33.7203	40.38	
5.3	15.0054	40.0810	40.0794	40.41	
14.4	13.4219	3.9633	34.9680	40.49	121.41
14.4	18.8881	50.3791	50.3860	40.46	
14.4	12.6470	33.7224	33.7203	40.47	
15.6	9.5049	25.3416	25.3407	40.48	121.47
15.6	13.6805	36.4610	36.4628	40.49	
15.6	13.6803	36.4610	36.4628	40.49	
18.8	13.5984	36.2088	36.2094	40.53	121.59
18.8	13.8618	36.9531	36.9566	40.53	
52.2	14.6212	38.9046	38.9098	40.56	121.71
52.2	15.0689	40.0810	40.0794	40.58	
55.7	13.7122	36.4610	36.4628	40.58	121.77
55.7	14.7014	39.0805	39.0816	40.59	
83.3	13.6305	36.2088	36.2094	40.63	121.89
83.3	14.9424	—	39.6998	40.61	
83.3	13.8998	36.9531	36.9566	40.64	

¹⁾ This result is decidedly too low, as a trace of antimony got lost during the washing.

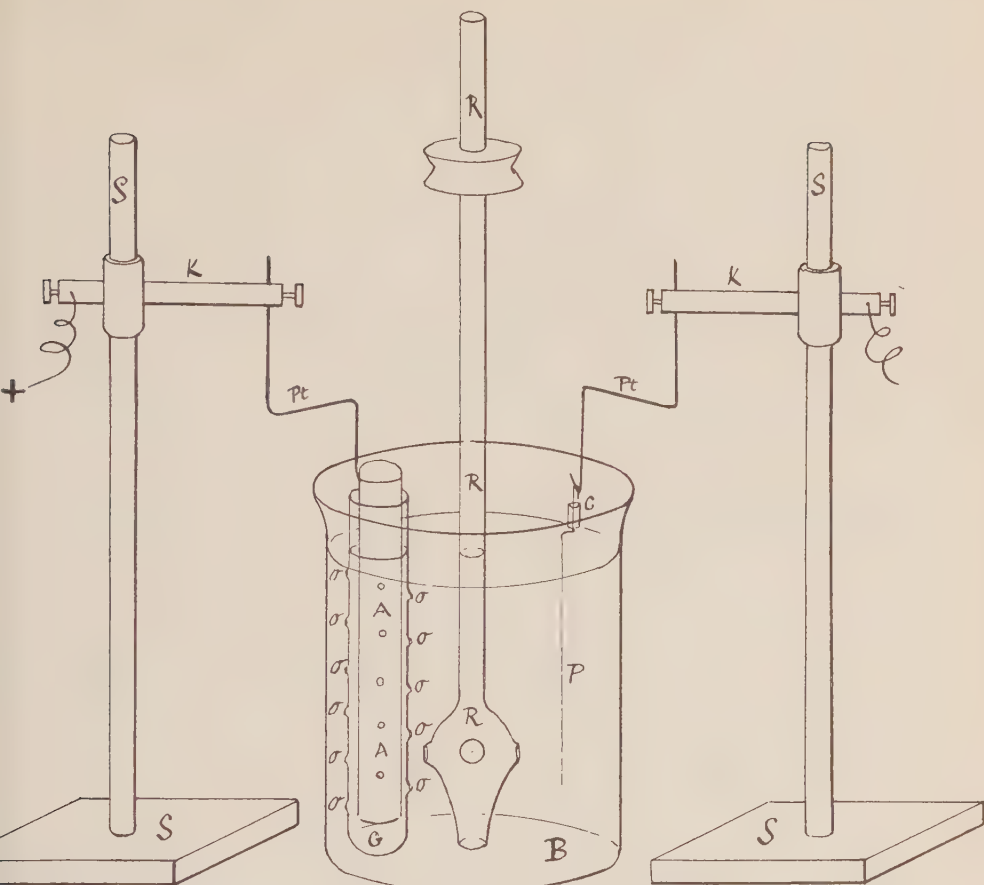


Fig. 1.

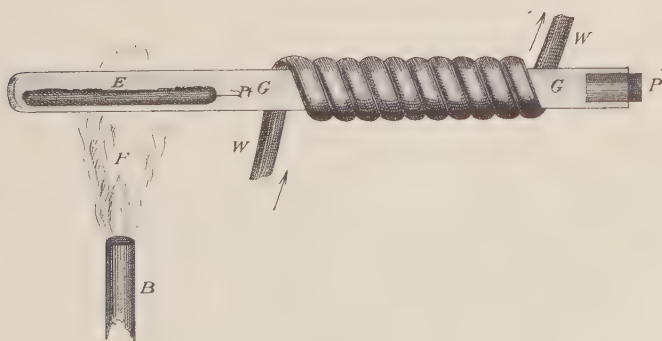


Fig. 2.

Chemistry. — “*The conductive power of hydrazine and of substances dissolved therein.*” By Prof. ERNST COHEN and Prof. C. A. LOBRY DE BRUYN. (Communicated by Prof. C. A. LOBRY DE BRUYN).

(Communicated in the meeting of February 28, 1903).

The investigation of the conductive power of non-aqueous solutions has of late years been known to have an increasing significance and particularly so on account of the important result that the laws and rules applying to aqueous solutions do not appear to apply in the case of other solvents. Apart from methyl and ethyl alcohol (the constitution of which does not differ much from the type water) sulphurdioxide, ammonia (NH_3), formic acid, hydrocyanic acid, pyridine, some nitriles, hydrogen peroxide and others have been studied as such¹).

The physical properties of free hydrazine²) N_2H_4 although still incompletely known, might lead us to suppose that this liquid would manifest a strong ionising power. In the first place, like water, the lower alcohols and acids, it possesses an abnormally high boiling point. This is obvious if this point (about 113° at 760 m.m.) is compared with of ammonia (-34°), difference of 147° , and if one considers that the difference between the boiling points of CH_3 and C_2H_6 is decidedly less (80°); this fact as well as the high critical temperature of (at least) 380° point to an association of the N_2H_4 molecules. The solubility of several alkali salts in hydrazine has also been shown to be very considerable although less than in water. Another existing observation points to the fact that hydrazine may, like ammoniac take the place of water of crystallisation³). And finally, the dielectric constant of hydrazine, which Prof. P. DRUDE (Giessen) had the kindness to determine at our request, has turned out to be rather high, namely, 53 at 22° . It is now a known fact that there exists a certain although sometimes remote parallelism between the dissociating power of a liquid on the one hand and the association of its molecules, the solvent power and the dielectric constant on the other hand. As according to the experiments of FRANKLIN and KRAUS and of CADY liquefied ammonia is an ionising solvent, this might also be expected in the case of hydrazine. From the experiments⁴) presently to be described it will be seen that such is the case.

¹) Compare JONES, Am. Ch. J. **25**. 232. KAHLENBERG, J. Phys. Chem. **5**. 339. WALDEN and CENTNERSZWER, Z. phys. Ch. **39**. 514, 557 e. by J. TRAUBE, Chem. Zt. **26**. 1071. (1902).

²) LOBRY DE BRUYN, Recueil des Travaux Chimiques des Pays-Bas. **15**. 174.

³) Ibid. 179.

⁴) Some preliminary determinations were already made in 1896. l. c. 179.

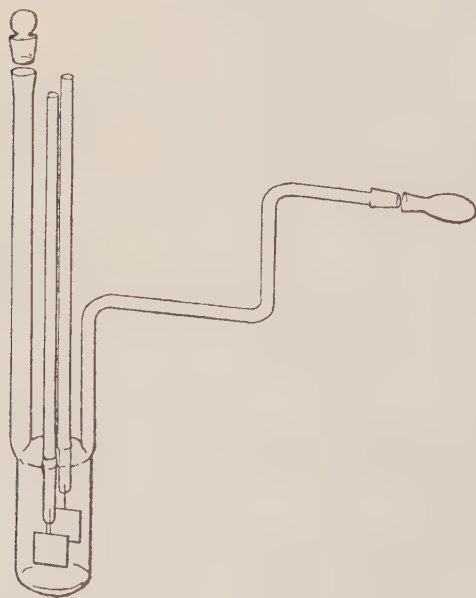
Let us first observe that the dielectric constant of hydrazine is only surpassed by those of five other liquids and is decidedly larger than that of NH_3 . We have namely:

hydrocyanic acid	95	acetonitrile	40
hydrogen peroxide	93	nitrobenzene	36.5
water	82	methylalcohol	32.5
formic acid	57	ammonia	22 (at -34°)
nitromethane	56.5	pyridin	20
hydrazine	53		

The peculiar properties of hydrazine (its very hygroscopic nature and liability to oxidation by atmospheric oxygen) demand great precautions in its preparation. It took place, according to the method already described ¹⁾, by treatment of the so-called hydrate with barium oxide and distillation in an atmosphere of hydrogen.

The heating with barium oxide and subsequent distillation were thrice repeated and the base was finally collected in six different fractions in pipette-shaped tubes in the manner previously described. During the last distillation the base had been only in contact with purified, dry hydrogen.

Apart from the properties of hydrazine mentioned, the high cost of the material was a factor which in our experiments had to be taken into account. A special apparatus (see illustration) was, therefore constructed which admitted of working with a small quantity of the base



(about 5.5 c.c.) and through which pure, dry nitrogen ²⁾ could be passed, whilst through the exit tube for the gas the weighed portions of the different salts could be introduced.

On account of the somewhat limited quantity of the base at disposal we could not, as is customary in the determination of the conductive power of solutions, start with the largest concentration and successively dilute this by adding the solvent, but the reverse was to be done.

¹⁾ l. c. p. 175.

²⁾ We take the opportunity to call attention to the fact that platinised electrodes

Weighed quantities of a salt were, therefore, successively dissolved; on account of the unavoidable errors in weighing it was difficult to experiment with very dilute solutions of accurately known composition, but by evaporating a measured quantity of a very dilute aqueous solution in a pipette which was then rinsed with the hydrazine we have reached for KCl a concentration of $V = \pm 900$.

In view of the above we wish to remark generally that our results cannot lay claim to very great accuracy, although they quite suffice even from a quantitative point of view, to prove that free hydrazine has a strong ionising power comparable with that of water.

We have worked with solutions of H_2O , KCl, KBr, and KJ and made a few experiments with a solution of Na and H_3N in $N_2 H_4$.

In the first experiment the six different fractions of the hydrazine had not been kept separate; as we had previously found ¹⁾ that the meltingpoints of the second and fourth fractions were the same we thought we might conclude that at least the middle fractions were similar. It then appeared, however, that the conductive power of the bases taken from different tubes often showed appreciable differences.

For this reason a second preparation was made and the hydrazine of each fraction (each time collected in several tubes) was examined separately as to its conductive power. From the following figures it appears that the conductive power gradually decreases and is smallest for the last fraction.

fraction n ^o . 2	κ at 25° = 18.10 ⁻⁵
3	12.8 "
4	11.2 "
5	10.0 "
6	6.5 "

We do not know what impurity (in any case very small) is the cause of this; possibly we are dealing here with a minute quantity of ammonia which is present in largest amount in the first fractions

The smallest conductive power observed by us in any fraction prepared previously was 4.10⁻⁵.

Our experiments have been mostly conducted with fraction N^o. 6 of the above-mentioned quantity.

dried in the air may occlude such an appreciable amount of oxygen that this must make its influence felt when working with readily oxidisable liquids. Such appeared to be the case when filling our apparatus with hydrogen when a spontaneous deposit of visible drops of water was formed.

²⁾ Prepared from air and phosphorus.

¹⁾ l. c. p. 177.

The apparatus was put into a glass vessel containing paraffin oil which was placed in an Ostwald thermostat; the temperature was 25°.

Hydrazine and water ($t = 25^\circ$)			
5 ^e fraction.	$G = 5.185.$	6 ^e fraction.	$G = 4.249.$
N.	κ	N	κ
0	$10.0 \cdot 10^{-5}$	0	$6.04 \cdot 10^{-}$
0.93	9.79 »	41.1	4.71 »
7.94	8.95 »	49.5	4.5 »
21.15	7.68 »	58.4	4.36 »
33.8	7.22 »	69.5	4.55 »
65.6	6.04 »	81.6	4.9 »
82.4	6.09 »	124.7	7.3 »
101.8	7.85 »		
156	10.51 »		
255.5	17.51 »		

Potassiumchloride.

$t = 25^\circ$		$\kappa = 6,2 \cdot 10^{-5}$		
G	g	V	κ	$\Lambda^1)$
5.369	0,0272	14.7	$7.0 \cdot 10^{-3}$	102.9
»	0,0157	25.4	4.2 »	103.7
»	0,0080	49.7	2.2 »	109.3
[± 5.4	0,00045	± 900	$1.2 \cdot 10^{-4}$	$\pm 107^2)$]

Potassiumbromide.

$t = 25^\circ$		$\kappa = 6,5 \cdot 10^{-5}$		
G	g	V	κ	Λ
5.350	0,0617	10.3	$10.05 \cdot 10^{-3}$	103.8
»	0,0329	19.3	5.66 »	109.2
»	0,0214	29.9	3.77 »	112.7
»	0,0105	60.7	1.965 »	118.9

¹⁾ Λ_∞ could not be determined, so that the degree of dissociation of the salts is not known. The Λ 's, however, agree in magnitude with those of the aqueous solutions of the same salts.

²⁾ This value, obtained in the manner described on p. 553, is as a matter of fact uncertain. It proves that a very minute quantity of a dissolved substance may increase the conductive power considerably.

Potassiumiodide.

G	g	V	$t = 25^{\circ}$	
			$\kappa = 5,6.10^{-5}$ N_2H_4	Λ
5.600	0,072	12.9	8.49.40 ⁻³	105.6
»	0,0493	18.8	5.79 »	108.8
»	0,0280	33.2	3.40 »	112.8
»	0,0129	72	1.64 »	118

G = weight of hydrazine in grams.

Λ = aequivalent conductive power.

g = weight of the salt in grams.

V = number of Liters, in which is dissolved one mol. of the substance.

κ = specific conductive power

κ for the water used = $0,28.10^{-5}$

Without committing a grave error the sp. gr. of hydrazine at 25° may be taken as 1.00.

It is already known that sodium dissolves in hydrazine with evolution of hydrogen¹⁾. Pure hydrazine ($\kappa=9,1.10^{-5}$) was introduced into the apparatus and two particles of sodium (weighing about 10 milligrams) were added.

The metal slowly dissolved with evolution of hydrogen and after solution was complete the specific conductive power appeared to have increased to 131.10^{-5} .

It seemed very peculiar that a powerful evolution of gas still went on after the sodium had dissolved, showing a decomposition of the hydrazine with formation of ammonia. This decomposition ceased as soon as the liquid was poured out of the apparatus; apparently it only takes place by contact with the platinum black present on the electrodes and is, therefore, quite comparable to the spontaneous decomposition of an alkaline solution of hydrogen peroxide exposed to the same influence.

Finally a few experiments were made with a solution of ammonia in hydrazine. The solubility of that gas at the ordinary temperature did not seem to be large; about 4.3 per cent of NH_3 is present in the saturated solution. After a few bubbles of ammonia had been absorbed in the hydrazine (with $\kappa = 5.2.10^{-5}$) the conductive power appeared to be but slightly increased ($\kappa = 6.9.10^{-5}$); this was also still the case after the liquid had been saturated with ammonia (about

¹⁾ l. c. p. 183. Dr. J. W. Ditt has found that an atom of hydrogen is replaced here; the NaH_3N_2 formed is a substance which on being exposed to the air causes a violent spontaneous explosion.

220 mgr. of H_3N in 4.920 gr. of N_2H_4 , $v = 0.38$, $\alpha = 9.10^{-5}$). It is known that on dissolving ammonia in water the conductive power is but very slightly increased.

From the foregoing we may draw the conclusion that, with regard to its ionising power, hydrazine is comparable to water.

As regards mixtures of hydrazine and water it may be observed that on addition of water the conductive power at first decreases reaching a minimum with a mixture of 60 mols. of H_2O to 100 mols. N_2H_4 (about 25 per cent of H_2O and 75 per cent of N_2H_4) then increasing again. This minimum, therefore, does not correspond with the composition $\text{N}_2\text{H}_4 + \text{H}_2\text{O}$, or the so-called hydrate.

Utrecht—Amsterdam, January 1903.

Chemistry. — “*The velocity of transformation of tribromophenol-bromine into tetrabromophenol.*” By Mr. A. H. J. BELZER ¹⁾. (4th Communication on intramolecular rearrangement, presented by Prof. C. A. LOBRY DE BRUYN).

(Communicated in the meeting of February 28, 1903).

BENEDIKT ²⁾ found in 1879 that tribromophenol brought into contact with bromine water is capable of exchanging a fourth hydrogen atom for bromine with formation of a tetrabromo-derivative. The study of this substance led him to the conclusion that one Br-atom occupies a peculiar position in the molecule; it is, in fact, the cause of a certain number of reactions in which that Br-atom is readily displaced. As moreover the new substance seemed to have lost the character of a phenol as shown by its insolubility in alkalis, BENEDIKT gave it the formula $\text{C}_6\text{H}_2\text{Br}_3.\text{OBr}$ and the name of tribromophenolbromine. BENEDIKT also noticed that, when melted under sulphuric acid, it passes into the already known isomeric tetrabromophenol, a true phenol which no longer contains a loosely bound Br-atom.

In his first publication BENEDIKT looked upon this transformation into tetrabromophenol not as an intramolecular displacement of atoms but as a process taking place between two mols of tribromophenolbromine; in a later communication however he does so, without stating any reasons.

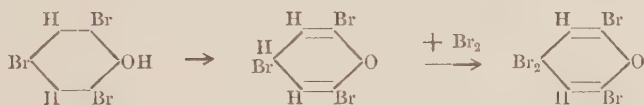
When a few years ago, JOH. THIELE ³⁾ found that BENEDIKT's

¹⁾ Proc. 31 May, 28 June and 25 Oct. 1902.

²⁾ Annalen **199**, 127, Monatshefte **1**, 361.

³⁾ Ber. **33**, 673 (1900).

tribromophenolbromine by means of leadacetate passed into 2.6 dibromoquinone, with substitution of 2 Br by O, he looked upon it as a dibromoquinone in which one O is replaced by 2 Br [therefore as a tetrabromoketodihydrobenzene]; he is of opinion that its formation from tribromophenol can only be explained by assuming that the latter can react in the tautomeric form of a p-quinoid ketone as follows:



In a paper which appeared a year ago, KASTLE ¹⁾ has come to the same conclusion as THIELE, as the result of investigations conducted conjointly with LOEVENHART, ROSA SPEIJER and GILBERT. KASTLE has also established the fact that it is only sulphuric acid which, even at the ordinary temperature, is capable of causing the transformation into tetrabromophenol; a dozen other reagents gave a negative result. In order to explain this specific action of sulphuric acid, KASTLE assumes the intermediate formation of an additive product of this acid with tribromophenolbromine; this at first would lose HBr_1 which would then again react at once with reformation of sulphuric acid and cause the migration of Br into the benzene nucleus. This interpretation of the transformation requires the appearance of two non-isolated and therefore hypothetical intermediate products and of three successive reactions.

Mr. BELZER has now studied the velocity of transformation of tribromophenolbromine. The circumstance that the first substance readily parts with an atom of bromine would lead to expect that its quantitative estimation would be possible in the presence of tetrabromophenol. It now appeared that the elimination of free iodine from hydriodic acid, also observed by KASTLE, takes place quantitatively; tribromophenolbromine may therefore be estimated in the presence of tetrabromophenol by titration.

At the commencement of the investigation the behaviour of the solid substance towards sulphuric acid was ascertained. If the crystals are covered with the ordinary 96 per cent acid it is noticed that they lose their yellow colour and become opaque and white; of solution in the acid taking place nothing can be perceived even by the aid of the microscope. No formation of striae can be observed; the whole phenomenon seems to be enacted within the solid substance commencing on the surface where the substance is in contact with

¹⁾ Amer. Ch. J. 27. 31. (1902).

the acid. If the velocity of transformation is measured under these circumstances it is no matter for surprise *firstly* that no reaction constant is found, *secondly* that the reaction coefficient constantly diminishes as the inner parts of the crystals get more and more inaccessible to the acid. As expected beforehand the experiment has shown that very small crystals or the powdered substance are, on account of the larger free surface, more rapidly transformed than the larger crystals. The continuation of the research will show that the transformation is monomolecular and must, therefore, be taken as a real displacement of atoms (perhaps of two displacements one of which takes place with very great velocity). It is a remarkable fact that there should take place inside the molecule of a solid substance a displacement of atoms, an internal change of equilibrium leaving the molecule intact, by mere contact with sulphuric acid, without there being any question of solution.

Although we could not expect to get reaction-constants for a heterogenous mixture of a solid substance and sulphuric acid, this should be duly the case when we worked in a solvent. Here however a difficulty occurred which at first threatened to put a stop to the further prosecution of the research. A solvent was wanted which had no action either on tribromophenolbromine or sulphuric acid. Acetic acid scarcely dissolved the first substance and chloroform appeared to dissolve only traces of 96 per cent sulphuric acid. It was finally decided to choose the latter solvent and to thoroughly shake the solution with sulphuric acid¹⁾. The experiment proved that on applying the formula of the first order, constant reaction-coefficients made their appearance. A first result was thus obtained; the transformation does not proceed bimolecularly.

Mr. BELZER has now studied the influence of the concentration of the sulphuric acid and the temperature.

In most of the experiments, 3 grams of the substance were dissolved in 150 cc. of pure chloroform²⁾, the solution strongly shaken with the acid and after definite times 25 cc. were titrated.

Use has been made of:

- a.* H_2SO_4 with about 36% SO_3 , *b.* H_2SO_4 with about 1% SO_3
- c.* equal volumes of *b* and *d.* *d.* 96 per cent H_2SO_4 .

In the following tables the results obtained are not given in the form of reaction-constants, but to make the matter more plain, the

¹⁾ A uniform emulsion is very soon obtained.

²⁾ The chloroform was agitated a few times with water, dried over calcium-chloride, shaken with strong sulphuric acid and redistilled; it was preserved in the dark.

times (T) are mentioned at which the transformation has proceeded halfway.

A. Influence of the Concentration of Sulphuric Acid.

$t = 25^{\circ}$. 0,5 cc. sulphuric acid.

	acid a	b	c	d
T.	5 min. 49 sec.	2 hours 57 m.	13 h. 40,5 m.	very slowly

$t = 25^{\circ}$. 1 cc. sulphuric acid.

	acid a	b	c	d
T.	too rapid	25 m. 44 s.	2 h. 38,5 m.	7 h. 45 m.

B. Influence of the Quantity of Sulphuric Acid.

$t = 25^{\circ}$. acid a.

	1 cc.	0.6 cc.	0.5 cc.	0.3 cc.
T.	too rapid	too rapid	5 m. 49 s.	3 h. 8 m.

$t = 25^{\circ}$. acid b.

	2 cc.	1.5 cc. ¹⁾	1.25 cc.	1 cc.	0.5 cc.	0.25 cc. ²⁾
T.	too rapid	too rapid	25 m. 44 s.	55 m. 20 s.	2 h. 57 m.	

$t = 25^{\circ}$. acid c.

	1.5 cc.	1 cc.	0.5 cc.
T.	1 h. 16 m.	1. 2 h. 32.4 m. 2. 2 h. 38.4 m.	13 h. 40.5 m.

C. Influence of the Temperature.

Acid a.

	0.5 cc.	0.3 cc.	0.2 cc.
T. at $t = 35^{\circ}$	—	6 m. 12.5 s. } ± 30 times	32 m. 33 s.
» 25°	5 m. 49 s. } ± 10 times	3 h. 8 m. }	—
» 15°	58 m. 45 s. }	—	—

Acid b.

	1 cc.	0.5 cc.
T. at $t = 35^{\circ}$	—	33 m. 56 s. } ± 4 times
» 25°	25 m. 44 s. } ± 2 times	2 h. 57 m. }
» 15°	1 h. 15 m. }	—

¹⁾ Transformation almost completed after 20 minutes.

²⁾ Not yet decomposed to the extent of 15 % after 21 hours.

	Acid c, 1 cc.	Acid d. 1 cc.
T. at $t = 35^{\circ}$	58 m. 10 s.	1 h. 53.6 m.
» 25°	2 h. 35 m.	7 h. 45 m.
» 15°	3 h. 27 m.	

From the results obtained it appears in the first place that the transformation is a monomolecular one and, taking into consideration the circumstances under which it takes place, must be considered as an intramolecular rearrangement of atoms.

To this conclusion the following observations may be added.

A. The influence of the concentration of the acid, the other circumstances being the same, is very great. The course of the figures leads to the idea that the active agent, the catalyser is not H_2SO_4 but SO_3 . Experiments were therefore made to ascertain how chloroform behaves towards the four acids employed. Whilst from ordinary 96 % acid (*d*) but very minute traces were dissolved, this amount was perceptibly larger with acid *c* and still larger with acid *b*, whilst acid *a* appeared to yield very much SO_3 to the chloroform ¹⁾.

The idea that SO_3 is the catalysing substance is consequently confirmed. The rapid decrease of the concentration of the acid is also in agreement with this idea; this velocity is therefore as it were a measure of the concentration of the SO_3 still present in a sulphuric acid of given concentration.

B. It is now also very plain that the quantity of the acid must have a great influence. As shown by its behaviour to acid *a*, chloroform may dissolve considerable quantities of SO_3 . On shaking with sulphuric acid of a lesser concentration, the amount of SO_3 which passes into the chloroform will consequently depend on the quantity of the acid. The equilibrium for the SO_3 which distributes itself between the chloroform and the sulphuric acid changes, as is known, with the relative quantities of the two liquids and with the temperature.

As a consequence of the view taken here, it must be assumed that ordinary 96 % sulphuric acid still contains a minute quantity, of free SO_3 -molecules. This view is admissible ²⁾ since it is known

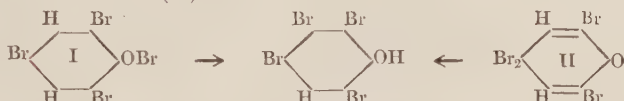
¹⁾ The ratio in which different acids yield SO_3 to chloroform will be further determined.

²⁾ KNIETSCH, in his well-known research on sulphuric acid, has shown that an acid of 97—98 % absorbs SO_3 much more readily than acids of smaller or larger concentration. From the results obtained up to the present it does not appear that, in the transformation of tribromophenolbromine, the 98 % acid *c* behaves in a particular manner; an extension of the research will elucidate this question.

that 100 % sulphuric acid contains a little SO_3 and consequently free H_2O .

C. The temperature-coefficient for sulphuric acid a is particularly large and increases rapidly with the temperature; for acid b it is decidedly smaller and very small for the 96 % acid. It will be readily understood that in the case of the acid a the dissociation of H_2SO_4 into SO_3 and H_2O and the distribution of SO_3 between chloroform and sulphuric acid are modified in a large degree when a change of temperature takes place.

The rearrangement of atoms may now be represented by the following schemes which respectively correspond with BENEDIKT's formula (I) and THIELE's formula (II):



Against the acceptance of THIELE's formule (II) it may be pointed out that in the displacement a Br atom must first remove an H atom; this then proceeds to the O atom with migration of the double bonds, a rather intricate process practically consisting of three succeeding displacements. As it has been proved that the reaction is one of the first order, two of those displacements must take place with immeasurable velocity. Against BENEDIKT's formula (I) may be remarked that, according to experience, the meta-position is hardly ever selected in the migration of an atom or of groups from the side chain into the nucleus.

The hypothesis proposed by KASTLE, which assumes the intermediate formation and decomposition of non-isolated products, is not at all supported by the observations communicated here.

The investigation as to the transformation of tribromophenolbromine will be completed and also extended to other analogous compounds.

Geology. — "*Some New Under-Cambrian Erratic-blocks from the Dutch Diluvium*". By J. H. BONNEMA. (Communicated by Prof. J. W. MOLL).

I. In the Geological-Mineralogic Institute at Groningen is found a piece of sandstone which a few years ago I found at Odoorn, in the province of Drente. With muriatic acid applied to it, there is no effervescence; consequently it does not contain any calcium-carbonate. The grains of sand are small, but with a magnifying glass they may be well distinguished. They are peculiarly lustrous.

The colour of this erratic-block is chiefly dark-grey. In some

places it is brownish. Moreover there are light-grey worm-shaped parts, varying in length and having a breadth of about 6 millimetres. This erratic-block is most probably a piece of Under-Cambrian sandstone, in which is found one of those problematical things that are sometimes called worm-passages. As they are not straight and do not run parallel to each other, they are different from those described as *Scolithus linearis* Hall. They show more resemblance with those tubes that were described by TORELL¹⁾ as *Scolithus errans* of Hardeberga and Andrarum. According to HOLST²⁾, however, there are various kinds of these worm-passages differing from *Scolithus linearis* Hall, whilst they also occur in different layers. This geologist makes mention of them as being found both in many places in the neighbourhood of Simrishamn and near Kalmar.

The Odoorn erratic-block bears no resemblance to the Hardeberga sandstone, in which *Scolithus errans* TORELL is found. MOBERG³⁾ writes that this sandstone shows a greyish-green colour, and that the worm-passages are dark-coloured. Nor does it resemble the Andrarum (Forsmölla) sandstone. According to TULLBERG⁴⁾ the latter is a white, quartziferous sandstone with yellow worm-passages.

The erratic-block also differs from the "Kråksten", which HOLST mentions, as being found near Kalmar, and which is greenish grey. From the kinds of sandstone with worm-passages which according to HOLST are met with in the neighbourhood of Simrishamn, differs that which occurs to the West of Raskarum in being whitish; and that which is found close by Ljunglyckorna is different because its worm-passages possess a dark colour. The sandstone which, according to this geologist, occurs to the North-West of Raskarum, may resemble, in colour, the Odoorn erratic-block: he says that its colour is sometimes a dirty-grey one. Unfortunately he does not tell his readers what is the colour of the worm-passages.

Consequently we cannot with certainty conclude whether this kind of sandstone still exists as firm rock, or not.

Nor have I been able to find anything whatever concerning the presence of suchlike erratic-blocks in the German and the Dutch diluvium.

1) TORELL, *Petrificata Suecana formationis cambriacae*. Lunds Univ. Årsskrift. 1869. Tom. VI. p. 12.

2) HOLST. *Beskrifning till kartbladet Simrishamn-Sveriges geologiska Undersökning*. 1892. Ser. Aa. N°. 109, p. 13.

HOLST. *Bidrag till kännedomen om lagerföljden inom den kambriska sandstenen*. Sveriges geologiska Undersökning, 1893. Ser. C. N°. 130, p. 6, 13, 14.

3) MOBERG. *Geologisk vägvisare inom Fogelsångstrakten*. 1896. p. 30.

4) TULLBERG. *Om Agnostus-arterna i de kambriska aflagringarne vid Andrarum*. Sveriges geologiska Undersökning. 1880. Ser. C. N°. 42, p. 3.

II. Some years ago I made an excursion in the surroundings of Murmerwoude in company with Mr. BOTKE, at the time a teacher at Murmerwoude, now a teacher at a secondary school at Nimeguen. To the West of this village, situated in the north-eastern part of the province of Frisia, we found in the sand that lay by the side of a freshly-dug canal two slab-shaped pieces of sandstone that fit each other exactly and must have formed one whole. The dimensions of the bigger piece are about 20, 10 and 4,5 centimetres. The other piece also possesses the two first-mentioned dimensions, but the third is 3 centimetres.

These pieces drew my attention as containing many more or less complete stone-kernels and off-prints of pyramidal Hyolithus-shells. The pointed ends of all these lie in the same direction, which must certainly be attributed to the influence of streaming water.

These erratic-blocks consist of hard, grey, very fine-grained sandstone. With muriatic acid applied to them there is no effervescence. Here and there they show small, yellow-brown spots. Some of the stone-kernels and that which lies close around them show the same colour.

The stone-kernels are straight and slowly increase in breadth. The dorsal side is flat or somewhat concave; at the mouth it is more or less convex. This side is not lengthened towards the front, so that we have here a specimen of the subgenus *Orthotheca*. With the exception of the dorsal side the surface of the stone-kernels is regularly vaulted. Consequently the transverse section is about circle-shaped, with only one segment cut off. Towards the pointed end they become more or less triangular. In one stone-kernel, which is not exposed to view in its full length, the visible part points to a length of about 35 millimetres and to a breadth, at the mouth, of 7 millimetres.

It appears from these properties that these stone-kernels originate from the Hyolithus (*Orthotheca*)-species, which has been described and pictured by HOLM¹⁾ as Hyolithus (*Orthotheca*) de Geeri.

HOLM tells us already that sandstone with Hyolithus de Geeri is Under-Cambrian. I have, however, not been able to find in his work, on what grounds this assertion is founded. Most probably he came to this conclusion because the nature of the stone points to it. At the time sandstone with Hyolithus de Geeri was not yet known as firm rock. Even now I have not been able to find in the books at my disposal, that sandstone with Hyolithus de Geeri should be known

¹⁾ HOLM. Sveriges Kambrisk-Siluriska Hyolithidae och Conulariidae. Sveriges geologiska Undersökning. Ser. C. No. 112. p. 54.

as such. As far as I can see this species of *Hyalolithus*, when Holm described it, had not been discovered in company with a fossil from which its age might be determined. MOBERG¹⁾ afterward found many specimens in a few big blocks of sandstone, which furnished him the material for the description of the new species of *Trilobites* called *Holmia Lundgreni*. The latter lay in the neighbourhood of lake Tunbyholm in the eastern part of the province of Schonen; according to MOBERG suchlike stone with remains of *Trilobites* occurs as firm rock not far from this place. As MOBERG informs us that sandstone with *Holmia Lundgreni* is older than that with *Holmia Kjerulfi* Linns, this was probably also the case with the sandstone-layers of which the Murmerwoude erratic-blocks formerly formed part.

It appears from MOBERG's description of the stone of the erratic-blocks with *Holmia Lundgreni*, that this stone in some respects resembles the material of which the Murmerwoude erratic-blocks consist. Both are very fine-grained and contain no calcium-carbonate. There does not seem to be much difference in colour either, at least as far as some parts of the Swedish erratic-blocks are concerned: MOBERG tells us that the sandstone described by him is chiefly of a bright light-grey colour, though sometimes showing small brown spots of ferrihydroxide. My erratic blocks, however, contain no pieces of phosphorite, which those from the neighbourhood of lake Tunbyholm do.

Besides the erratic-blocks spoken of just now, others of sandstone with *Hyalolithus* de Geeri-remains were also found, as Holm tells us, in the province of Schonen, near Simrishamn and Köpinge.

The same author makes mention of suchlike stones having been gathered near Rüdersdorf not far from Berlin, and near Bützow in Mecklenburg. It follows from the descriptions he gives of these pieces, that petrographically they bear no resemblance to those found at Murmerwoude. The latter are least different from the erratic-block found by Prof. DE GEER at Rüdersdorf. My pieces, however, contain no particles of glimmer.

No more have corresponding erratic-blocks of *Hyalolithus*-sandstone been found in any part of the Netherlands. The first of this kind of stone were made mention of by VAN CALKER²⁾. They originate from Steenberg in the northern part of Drente; they are three stones

1) MOBERG. Sveriges älsta kända *Trilobiter*. Geol. Fören. in Stockholm förhandlingar 1899. Bd. 21. Häft 4. p. 324.

2) VAN CALKER. Ueber ein Vorkommen von Kantengeschieben und von *Hyalolithus*- und *Scolithus*-Sandstein in Holland. Zeitschr. d. Deutsch. geol. Gesellschaft. Jahrg. 1890. p. 581.

resembling each other. From the description VAN CALKER gives of the stonekernels occurring in them, HOLM already drew the conclusion that they originate from *Hyalolithus de Geeri*. These erratic-blocks consist, however, of dark asch-grey sandstone, so that they differ in colour from the Murmerwoude ones.

Afterward two more pieces of *Hyalolithus*-sandstone were mentioned by me¹⁾. One was found at Kloosterholt (Heiligerlee), the other at Roden, in the North of the province of Drente. The former is a small piece of fine-grained sand-stone, yellow-grey on the inside and brownish on the outside, in which are found some fragments of stone-kernels of *Hyalolithus*-shells. A few of these fragments are entirely dark-brown, others have a light-grey surface. One of the stone-kernels shows the transverse section characteristic of *Hyalolithus de Geeri*. The Roden erratic-block is rather a large slab of sandstone, containing especially off-prints of pyramidal *Hyalolithus*-shells. This one is reddish on the inside and light-grey on the outside.

Where the sandstone-layers of which the Murmerwoude erratic-blocks in former times formed part, were originally found as firm rock, cannot be said with certainty, as appears from what was written above. Most probably it was near the western coast of the southern part of Sweden.

III. That the knowledge of our sedimentary erratics still leaves so much to be desired, must certainly be partly attributed to the fact that so few of them have been gathered up to this time. Non-geologists, too, by their researches, may deserve well of this branch of knowledge, as was proved once more by Prof. Dr. J. C. KAPTEYN, filling a chair at the Groningen University.

This well-known Astronomer, who in summer lives at Vries, in the northern part of Drente, last summer searched the surroundings of this village for sedimentary erratic-blocks. To his researches we owe a piece that is certainly the most interesting of the erratics described here.

Just outside this village, by the road leading to Donderen, was found a small, slab-shaped erratic-block three centimetres thick, the largest dimension of which is 14 centimetres. It consists of sandstone coloured yellow-grey by ferrihydroxide. At the surface it is brownish. With muriatic acid there is no effervescence. The grains of sand

¹⁾ BONNEMA. De sedimentaire zwerfblokken van Kloosterholt (Heiligerlee). Versl. v. d. Koninkl. Akad. v. Wetenschappen 1898. p. 450.

VAN CALKER, Ueber eine Sammlung von Geschieben von Kloosterholt. Zeitschr. d. Deutsch. geol. Gesellsch. Jahrg. 1898. p. 234.

are for the greater part very small; they are not easily distinguished. Among them are bigger transparent ones. The diameter of these latter grains is at most $\frac{1}{2}$ millimetre; they are mostly arranged in parallel planes, in consequence of which an indistinct layer-like construction becomes visible on the vertical sides. On one of the horizontal sides there are still parts of a few thin layers. In the stone are a great many small cavities, which were formerly evidently filled with organic remains.

On both of the horizontal sides we find remains of Tribolites. On one of them the most important are an off-print of a mid-shell about 8 millimetres long, and a stone-kernel 10 millimetres long, part of the shell of which, turned into iron-hydroxide, is still present. On the other horizontal side is found the front part of an off-print of a much larger mid-shell, which once had a length of about 15 millimetres.

Undoubtedly these remains, which in many respects resemble each other, have come from the same kind of Tribolites. The two first mentioned are remains of younger individuals; the other belonged to a more or less full-grown specimen.

With the younger individuals the glabella was convex, its length surpassed its breadth a little, its breadth diminishing towards the front. On the front side the glabella is somewhat rounded. On the plaster-cast I made of the off-print of the small mid-shell, it is clearly visible that the glabella possessed at least 2 side-furrows on either side. The stone-kernel shows that the neck-ring was broadened in the middle. The cheeks were vaulted, which is very clear in the stone-kernel especially. Very characteristic is a deep furrow enclosing the glabella in front and being continued on either side on the cheeks, where it broadens and becomes less deep. Before this furrow is a vaulted part, which does not turn down. The front-edge of this part is on about the same level with the back-edge, whilst its height is equal to that of the glabella. In the off-print of the little mid-shell the glabella is $4\frac{1}{2}$ millimetres in length, and the part in front of it nearly 3 millimetres in breadth.

It is apparent from the off-print of the mid-shell of the more or less full-grown animal, which mid-shell is only partly exposed to view, that the glabella and that part of the mid-shell which is in front of it, which does not turn down here either, are less vaulted, and that the furrow separating the two, is less deep. Here are no side-furrows to be distinguished on the glabella.

With the assistance of the scientific works I dispose of, I found that these remains are most like those of *Arionellus primaevus* BRÖGGER, of which up to this time only mid-shells have been pictured and

described. The first pictures were given by KJERULF¹, after remains of the "grøn skifer" from Tomten (Tömten?) in Norway. He informed us already that they came from an *Arionellus*-species. Later on they were described by BRÖGGER²), who by them was induced to assume the new species *Arionellus Primaevus*. Under this head he also ranged the mid-shell that had been pictured by KJERULF in fig. 6. Afterward LINNARSSON³) pictured and described remains of this *Tribolite*. He moreover tells us that the mid-shell pictured by KJERULF as fig. 6 rather seems to belong to a new species called *Ellipsocephalus Nordenskiöldi*, instituted by him in the same essay. His material had been got from the "gråvacke-skiffern" of Forsemölla near Andrarum. He dared with certainty to range under the head *Arionellus Primaevus* a small mid-shell 5 millimetres long, which had been found in a sandstone-like variety of the stone mentioned above. This was not the case with mid-shells from the ordinary stone, which are about 15 millimetres long. He gives as his reasons for not daring to range these latter among *Arionellus Primaevus* BRÖGGER: first that they are much flatter, secondly that the furrows are much shallower, thirdly that the glabella has no side-furrows, fourthly that the glabella towards the front considerably diminishes in breadth. Why, notwithstanding all this, he at first ranged them under this head, though he had never heard of transition-forms, he explains by saying that BARRANDE had found exactly the same difference between the old and the young specimens of the Bohemian species *Arionellus Ceticcephalus* Barr., of which transition-forms are known.

The very same points of difference occur in the *Trilobites*-remains of the erratic-block found at Vries. Here, however, the glabella of the older specimen does not diminish in breadth more considerably than that of the younger individuals.

As I wished to be as certain as possible in my determination, I wrote to Prof. MÖBERG, director of the Geological Institute at Lund, to ask whether there was any material for comparison at my disposal there. Remains of this species of *Trilobites* seem to be very rare at Forsemölla, however, so that my request could not be complied with. I received as a present, however, a mid-shell of the *Ellipsocephalus Nordenskiöldi*, which seem to occur more frequently there, Prof.

¹) KJERULF „Sparagmitfjeldet". Universitetsprogram Kristiania. 1872. p. 81. Fig. 7—9.

²) BRÖGGER, Om Paradoxidesskifrene ved Krekling. Nyt Magazin for Naturvidenskaben. 1878. Bd. 24. p. 58.

³) LINNARSSON, De undre Paradoxideslagren vid Andrarum. Sveriges geologiska Undersökning 1882. Ser. C. N^o. 54. p. 21. Taf. IV. fig. 3, 4.

MOBERG supposing that my Trilobites-remains would prove to belong to this species, which is not always to be distinguished from *Arionellus Primaevus*.

Indeed, I had been thinking of this species, but as LINNARSSON declares that here the vaulted part of the mid-shell before the glabella towards the outside slopes strongly down, I thought I could not range my remains under this head. The mid-shell I received from Lund confirmed my opinion. I informed Prof. MOBERG of this and sent him a few plaster-casts of the Trilobites-remains occurring in the erratic-block found at Vries. I was answered that Prof. MOBERG shared my opinion and considered them as having come from *Arionellus Primaevus*. At the same time he was so kind as to send me a plaster-cast of the best of the mid-shells of this species of Trilobites, found in the collection at Lund. Now I could ascertain that in *Arionellus Primaevus* the part of the cephalon in front of the glabella does not turn down, which is not specially mentioned by BRÖGGER and LINNARSSON.

Also in the mid-shell of which MOBERG sent me a plaster-cast, the breadth of the glabella diminishes but little towards the front, though its length is about 14 millimetres.

I think, then, that we now may with certainty conclude, that in the Vries erratic-block we find remains of *Arionellus Primaevus* BRÖGGER. As this Trilobite occurs only in layers that contain remains of *Holmia* (*Olenellus*) *Kjerulfi* LINRS, and as these are taken to be the youngest of the Under-Cambrian ones, the age of the layer of which this erratic-block in former times formed part, may be easily determined.

Besides occurring at Tömten in Norway and at Forsemölla near Andrarum in Schonen, which places I mentioned already, *Arionellus Primaevus* is probably found in two more places in firm rock, viz. at Kiviks Esperöd to the North and at Gislöfs Hammar to the South of Simrishamn in Schonen. The former place was first made mention of by NATHORST¹⁾, who told that he had found there an off-print of an *Arionellus*? That in Gislöfs Hammar remains of an *Arionellus* occur, was first communicated to us by LINNARSSON, in his description of the *Arionellus*-remains of Forsemölla. According to this writer, many of the mid-shells found there by VON SCHMALENSEE much resembled the larger shells of Forsemölla, which he dared not with certainty call *Arionellus Primaevus*.

¹⁾ NATHORST. Om de kambriska och siluriska lagren vid Kiviks Esperöd etc. Geol. Föreningens i Stockholm Förhandlingar. Bd. 3. 1877. p. 264.

As for two kinds occurring in the same place, HOLST ¹⁾ mentions that the "gråvackeskiffer" may also contain a species of *Arionellus* (*Arionellus Primaevus* BRÖGGER ?).

From communications made by TULLBERG ²⁾ and HENNIG ³⁾ the conclusion might be drawn that *Arionellus Primaevus* BRÖGG occurring at Kiviks Esperöd and Gislöfs Hammar, had been sufficiently indicated. I think, however, that this should not be done. The list of fossils which these two authors have drawn up with regard to the "gråvackeskiffer" of the two places mentioned just now and of Andrarum, must refer, in my opinion, to these places taken collectively and not to each separately. I am confirmed in this opinion by the fact that remains of *Holmia Kjerulfi* LINRS (or of a kindred species) are not mentioned by MOBERG ⁴⁾ as being found at Kiviks Esperöd, whereas they are mentioned by them.

The origin of this erratic-block must most probably be looked for in the eastern part of Schonen or in the Baltic Sea-region bordering on it. That petrographically it differs from the ordinary "gråvackeskiffer", does not clash with this opinion, several writers informing us that the latter often changes into sandstone. The thin layers on the lower side indicate that something of the kind has been the case here.

It is not likely to have come from Norway, for never was a sedimentary erratic-block found in these parts, of which this may be said.

As was mentioned above, I take this erratic-block to be the most interesting one of the pieces that are described in this paper. I do this because it is the first piece coming from layers with *Holmia Kjerulfi* LINRS that has ever been made mention of. Nowhere in literature did I find anything about an erratic-block of that age.

IV. Shortly before the summer-holidays of last year I found, when visiting the loam-pit close by Hemelum, a slab-shaped piece of fine-grained sandstone three centimetres thick, whilst its largest dimension is a little more than 20 centimetres. It is layered and contains calcium-carbonate, so that with muriatic acid it gives effervescence of dioxide-carbonate.

Owing to the large number of Glauconite-grains it contains, the

¹⁾ HOLST. Beskrifning till kartbladet Simrishamn, p. 17.

²⁾ TULLBERG, Skånes Graptoliter. I. Allmän öfversigt öfver de siluriska bildingarne i Skåne och jemförelse med öfriga kända samtidiga aflagrningar. Sveriges geologiska Undersökning, 1882. Ser. C. No. 50. p. 26.

³⁾ HENNIG, Geologischer Führer durch Schonen. 1900. p. 26.

⁴⁾ MOBERG, Sveriges älsta kända Trilobiter.

stone of which this erratic-block consists is coloured a strong green. This is the case with some layers especially. Some particles of a light-coloured kind of glimmer are found in it.

My attention was drawn to this kind of sandstone, because, when splitting this erratic-block into two parts, I found that it contains Hyolithus-remains, viz. grey-coloured stone-kernels. The lower part of one of them is brown.

When visiting the Natural History-Museum at Hamburg last summer, and admiring its collection of sedimentary erratic-blocks, I asked Prof. GOTTSCHÉ whether he knew of suchlike erratics. Prof. GOTTSCHÉ thought he remembered such pieces to have been found in the surroundings of Hamburg. Owing to want of exposing-room, however, they lay packed up among other pieces, in consequence of which they could not be shown me. He drew my attention to the fact that in this kind of erratic-blocks sometimes occur small conical valves of horn-shelled Brachiopodes. These valves were shown to me in a brown-coloured erratic-block.

A short time after I found on the beach at Borgholm in Oeland not only an erratic-block with Hyolithus-rests entirely corresponding with my Hemelum piece, but also a brown piece of sandstone with a valve of a small horn-shelled Brachiopode.

I searched my books for anything on the subject of this kind of erratics or stone, but at first without any result.

As Prof. MOBERG at Lund in the summer of 1901, when I had requested him to be so kind as to give me some information concerning Oeland, had noted down on my map of this island that on its coast, to the North of Färjestaden, occur erratic-blocks with Discinella Holsti (then unknown to me), and the valves of Brachiopodes I had found were, like those of Discina, horny and flat-conical, but much smaller, I supposed that Prof. MOBERG could give me some information about this stone. For this reason I intended to write to him concerning this subject, and, was going to do so, when accidentally I discovered in the essay of HOLM¹⁾ on the Swedish Hyolithidae and Conulariidae, that by MOBERG²⁾ a greenish kind of sandstone, rich in Glauconites, with Discinella Holsti MOBERG and Hyolithes, occurring as erratic-blocks in Oeland, had been described.

Having studied MOBERG's essay, I find that the stone of which my

1) HOLM. SVERIGES Kambrisk-Siluriska Hyolithidae och Conulariidae. SVERIGES Geologiska Undersökning. Ser. C. No. 112.

2) MOBERG. Om en nyupptäckt fauna i block of kambrisk sandsten, insamlade of dr. N. O. HOLST. Geologiska Föreningens i Stockholm Förhandlingar 1902. No. 142. Bd. 14. Häft 2. p. 103.

erratic-blocks with Hyolithus-remains consist, has been described by this author as type *a*. The piece of brown sandstone with the valve of a small Brachiopode I found at Borgholm, belongs to his type *d*. The fossil occurring in it has been determined by me as a vaulted valve of *Discinella Holsti* MOBERG. The erratic-block that was shown me by GOTTSCHÉ probably belongs to the same type; the organic remains occurring in it are likely to have come from the same species of Brachiopodes.

The Hyolithus-remains in the Hemelum erratic-block have been very imperfectly preserved, which, according to HOLM,¹⁾ is usually the case with this stone. A longitudinal section possesses a length of 10 millimetres and at the mouth a breadth of 4 millimetres, so the dimensions of this shell remind of the one pictured and described by MOBERG²⁾ under the name of *Hyolithus Insularis* nov. spec., whereas HOLM afterward called it *Hyolithus Confusus* nov. spec.

The relative age of this kind of erratic-blocks does not seem to be with certainty known yet, as up to this time no corresponding stone has been met with as firm rock, and the organic remains found in them have not yet been discovered in company with such as might contribute to the solution of this question. MOBERG, however, thinks he may conclude from the general character of the fossils occurring in them, from their petrographical nature and from the way in which they are spread, that they come from Under-Cambrian layers.

HOLST³⁾ draws the same conclusion, after tracing the manner in which they are spread. I think I may infer from his essay, that in his opinion they come from the youngest Under-Cambrian layers. In accordance with this is the presence of *Discinella*-remains, this genus of Brachiopodes occurring, according to MOBERG, in North-America, in layers containing *Olenellus*.

As was said just now, a corresponding kind of stone was not yet met with as firm rock. Most probably it formerly occurred westward of Oeland; it may be found there even now at the bottom of the sea, because this kind of erratic-blocks is found in large numbers only on the western coast of this island, between Halltorp and Mörbylånga, and on the little isles and cliffs in the neighbourhood. Less numerous they are in the other parts of the eastern and western coasts of the Kalmarsund.

1) HOLM loc cit. p. 74.

2) MOBERG. Om en nyupptäckt fauna i block of kambrisk sandsten etc. p. 117.

3) HOLST. Bidrag till kännedomen om lagerföljden inom den kambriska sandstenen, p. 9.

MOBERG says that these erratics were found by Dr. HOLST on Bornholm, too. Neither in German nor in Dutch literature have I been able to find anything concerning suchlike erratic-blocks. It is almost doubtless, however, that they are mentioned by GOTTSCHÉ¹⁾ as "Cambrische Grauwackeschiefer". Only those erratic-blocks which, according to him, resemble the Swedish "Gråwackeskiifer", must be taken into consideration then. The description of the latter entirely corresponds with that of type *a* by MOBERG. The small, round, horny-lustrous Brachiopodes-valves with a diameter of 2 millimetres, mentioned by GOTTSCHÉ, which may come from *Discinella Holsti* MOBERG, also cause us to conclude that we have the same kind of stone here. GOTTSCHÉ does not inform us of Hyolithus-remains occurring in suchlike erratic-blocks. No erratics containing them had perhaps been found at the time. It follows from what he orally communicated to me, that now they have most probably been found.

The same author says that according to LINNARSSON a kind of stone entirely corresponding with the one described by him, has been met with by HUMMEL near Tereskov (wich HUMMEL calls Torekov), on the coast of N. W.-Schonen, as firm rock. Judging from the description HUMMEL²⁾ gives of it, it much resembles, petrographically, type *a* of the *Discinella Holsti*-sandstone. HUMMEL does not say, however, that fossils are found in it. Perhaps we have here the same case as with the Glauconitic sandstone from the neighbourhood of Simrishamn, of which HOLST³⁾ writes that a corresponding kind frequently occurs in the "sandstone-region" of the Kalmarsund. Here, too, the resemblance seems to be petrographic at best, for MOBERG, in his essay, speaks about this sandstone no more than about that of TOREKOV.

Most probably the thin-layered, greenish stone which resembles the "Grauwacken-Schiefer" of the *Olenellus Kjerulfi*-region, and which petrographically keeps the medium between the *Olenellus*-stone of Hardeberga in Schonen and the equally old "grön skiffer" of Bornholm, with stone-kernels of a Brachiopode probably belonging to *Acrothele*, and with Hyolithus-remains bearing the greatest resemblance to *Hyolithus Lenticularis* Holm, as STOLLEY⁴⁾ writes, — is also *Discinella Holsti*-sandstone.

1) GOTTSCHÉ. Die Sedimentär-Geschiebe der Provinz Schleswig-Holstein. 1883. p. 8.

2) HUMMEL. Beskrifning till kartbladet „Båstad". (No. 60). SVERIGES geologiska Undersökning. 1877. p. 10.

3) HOLST. Beskrifning till kartbladet Simrishamn. p. 15.

4) STOLLEY. Die cambrischen und silurischen Geschiebe Schleswig-Holsteins. Archiv für Anthropologie und Geologie Schleswig-Holsteins und der benachbarten Gebiete. 1895. Bd. I. Heft. 1. p. 130.

Finally I must mention that, on the occasion of a later visit to the loam-pit near Hemelum, I found two more erratic-blocks, which must probably also be counted among pieces of Discinella Holstisandstone. Neither contains any fossils. One corresponds petrographically with what was described; the other is for the greater part white, but possesses green layers. If I am not mistaken, I sometimes saw suchlike stones on the beach of Borgholm.

Physics. — “*On the course of the values of b for hydrogen, in connection with a recent formula of Prof. VAN DER WAALS.*”

By Dr. J. J. VAN LAAR. (Communicated by Prof. J. D. VAN DER WAALS).

1. Making use of the theory of *cyclic* motions, Prof. VAN DER WAALS has given a new deduction of the equation of state of a simple substance, in which the size of the molecule appeared to be variable, and to be a function of the *volume*¹⁾.

For a bi-atomic gas the following formula has been found:

$$\frac{b-b_0}{v-b} = 1 - \left(\frac{b-b_0}{b_g-b_0} \right)^2 \cdot \cdot \cdot \cdot \cdot \quad (1)$$

Here b_0 denotes the smallest value of b , corresponding to the case that the two atoms of a molecule touch each other; b_g represents the greatest value i.e. the value for very great (infinitely great) volume. The above equation may be easily derived from the so called “equation of state of the molecule”:

$$\left[p + \frac{a}{v^2} + \alpha(b-b_0) \right] (b-b_0) = RT, \cdot \cdot \cdot \cdot \cdot \quad (a)$$

when we take $v = \infty$, in which case b assumes the value b_g and

$p + \frac{a}{v^2}$ may be neglected with respect to $\alpha(b-b_0)$. So we get:

$$\alpha(b_g-b_0)^2 = RT.$$

If we substitute this value into equation (a), paying regard to

$$p + \frac{a}{v^2} = \frac{RT}{v-b},$$

we get the equation

$$\left(\frac{1}{v-b} + \frac{b-b_0}{(b_g-b_0)^2} \right) (b-b_0) = 1,$$

which yields immediately equation (1).

¹⁾ These Proceedings of the meetings of February, March and April 1901. See also “*Livre jubilaire dédié à J. BOSSCHA*” of the Arch. Néerl., p. 47. (The first communication and part of the second discuss principally the specific heat for very large volume).

The quantity a in the equation of state (a) depends on the forces, which keep the atoms together in the molecule. These forces are supposed to be proportional to the linear deviation from the position of equilibrium $r-r_0$.

The equation of state (a) for a tri-atomic gas, e. g. CO_2 — which in this case is the combination of two similar equations — will contain besides RT still a factor f , whose value will vary from 1 to 2 according as the different cases occur, which we may distinguish in the motion of the atoms. For CO_2 a value of nearly 2 is found for f . As, however, this quantity f for a certain substance is, strictly speaking, variable (see the paper in the “*Livre dédié à BOSSCHA*”, quoted above) and as the accurate equation is therefore very complicate, I have chosen a bi-atomic gas, namely hydrogen, in order to test the new equation of VAN DER WAALS. In this case $f=1$ and the relation between b and v is represented by the simple equation (1). I hope later to test the equations for oxygen and nitrogen, in order to examine whether the results found for hydrogen also hold for these gases.

II. An *accurate* knowledge of a is required for the exact calculation of b . This is still a great difficulty. *Absolute* certainty as to this value cannot be obtained as yet, but still it appears to me that the value $a=300 \times 10^{-6}$ ¹⁾ has a high degree of probability. Assuming another value for a , I found namely that the values calculated for b decrease much too rapidly, — much more rapidly than agrees with formula (1); this is principally the case in the beginning, i. e. for large values of v . Only the values of b , calculated for $a=300 \times 10^{-6}$ varied in such a way, that their course was represented by equation (1) with nearly perfect accuracy. SCHALKWIJK ²⁾ also calculated from his last experiments $10^6 a = 300$ ($10^6 b_g = 910$). I therefore thought myself justified in assuming 300 for $10^6 a$. In the following table we find the values for b at 0° Centigrade, calculated from the equation

$$\left(p + \frac{a}{v^2}\right)(v-b) = (1+a)(1-b)(1+at).$$

For $(1+a)(1-b)$ we put 0,9994. All values have been multiplied by 10^6 ; the same will be the case with all values of b which we give in what follows.

At 0° C. we have:

$$v-b = \frac{0,9994}{p + \frac{a}{v^2}}.$$

¹⁾ All values of v , b , etc. have been expressed in the usual practical units.

²⁾ These Proceedings, June 1901, p. 124.

0° C.

p	v^1	v^2	$\frac{a}{v^2}$	$v-b$	b found.	b calculated from (1)	Δ
100	10690	114.3	2.6 ²	9739	951	907	+44
150	7353	54.07	5.5 ⁵	6425	928	901	+27
200	5690	32.38	9.2 ⁶	4777	913	396	+17
250	4692	22.01	13.6 ³	3791	901	891	+10
300	4030	16.24	18.4 ⁷	3138	892	886	+6
350	3560	12.67	23.6 ⁸	2675	885	880	+5
400	3207	10.28	29.1 ⁸	2329	878	875	+3
450	2933	8.602	34.8 ⁷	2061	872	870	+2
500	2713	7.360	40.8	1848	865	865	± 0
550	2533	6.416	46.8	1675	858	860	-2
600	2386 ⁵	5.695	52.7	1531	855	855	± 0
650	2259	5.103	58.8	1410	849	850	-1
700	2149 ⁵	4.620	64.9	1307	843	845	-2
750	2053	4.215	71.2	1217	836	840	-4
800	1971	3.885	77.2	1139	832	835	-3
850	1897	3.599	83.4	1071	826	830	-4
900	1833 ⁵	3.362	89.2	1010	823	826	-3
950	1774	3.147	95.3	956	818	821	-3
1000	1722 ⁵	2.967	101.1	908	815	817	-2
1100	1637	2.680	111.9	825	812	809	+3
1200	1557 ⁵	2.426	123.7	757	801	801	± 0
1300	1491	2.223	135.0	696	795	793	+2
1400	1432	2.051	146.3	646	786	785	+1
1500	1380	1.904	156.3	603	777	777	± 0
1600	1334 ⁵	1.781	168.4	565	769	770	-1
1700	1294 ⁵	1.681	178.5	532	762	763	-1
1800	1258	1.583	189.5	502	756	756	± 0
1900	1225	1.501	199.9	476	749	749	± 0
2000	1194 ⁵	1.427	210.2	452	742	743	-1
2100	1166 ⁵	1.361	220.4	431	736	736	± 0
2200	1141	1.302	230.4	411	730	730	± 0
2300	1118	1.250	240.0	393	725	724	+1
2400	1097 ⁵	1.205	249.0	377	720	719	+1
2500	1078	1.162	258.2	362	716	714	+2
2600	1059 ⁵	1.123	267.1	349	711	710	+1
2700	1042	1.086	276.2	336	706	705	+1
2800	1024 ⁵	1.050	285.7	324	701	700	+1

¹) Up to 1000 atmospheres the values of v have been borrowed from the results of the "second method" of AMAGAT (méthode des regards); from 600 atm. to

The values of v have been borrowed from the well known experiments of AMAGAT¹⁾.

The too large values of b in the beginning — here only to about 300 atm. — are still present. This indicates probably that the value $a = 300$ is still slightly too great. But from 300 atm. upwards the agreement is quite satisfactory. Small inaccuracies in the determination of the value of v have for large volumes a great influence on the values of b . To this circumstance also it may be ascribed that the values of b are in the beginning not reliable. So the value $v = 10690$ at $p = 100$ cannot be accurate to a higher degree than to ten units at the utmost. So it might also have been 10680 or 10670 and b or $v - (v - b)$ might have been 10 or 20 units smaller. The values of b "calculated" have been determined with the aid of equation (1) in the assumption

$$\underline{b_g = 917} \quad ; \quad \underline{b_0 = 463}.$$

b_0 may be determined in the following way. If we substitute into (1)

$$\frac{b - b_0}{b_g - b_0} = x,$$

and pay regard to $b - b_0 = \frac{x}{1-x} (b_g - b)$, then we get for (1):

$$\frac{x}{1-x} \frac{b_g - b}{v - b} = 1 - x^2,$$

and therefore:

$$\frac{b_g - b}{v - b} = \frac{1-x}{x} (1 - x^2).$$

For an assumed value of b_g this equation enables us to determine the corresponding value of x from v and b at e.g. 500, 1000, 1600, 2200, 2800 atm. The value of b_0 may then be calculated from

$$b_0 = b - (1 - x^2) (v - b),$$

which follows immediately from (1). So I found with $b_g = 917$ at 1000, 1600, 2200, 2800 atm. respectively the values $b_0 = 455, 463, 462, 466$. If we put $a = 400$ instead of $a = 300$, then we find with $b_g = 1000$ at $p = 2800$ atm. in the same way $b_0 = 463$. With

1000 atm. the values of v at 600, 700, 800, 900 and 1000 atm. represent the mean values of the results of the first method (that of the electrical contacts) and those of the second method. From 1100 atm. upwards the values of v have been determined by the first method.

¹⁾ Mémoires sur l'élasticité et la dilatabilité des fluides jusqu'aux très hautes pressions, p. 32-33 and 38.

$\alpha = 500$, $b_g = 1100$ we find at 2800 atm. again $b_0 = 464$. So we may assume with perfect certainty b_0 to differ very little from 463.

With this value of b_0 in the first place b_g was again calculated. From (1) follows:

$$\frac{(b-b_0)^2}{(b_g-b_0)^2} = 1 - \frac{b-b_0}{v-b} = \frac{(v-b) - (b-b_0)}{v-b},$$

so

$$b_g - b_0 = (b - b_0) \sqrt{\frac{v-b}{(v-b) - (b-b_0)}}.$$

In this way I found at $p=500, 600, 700, 800, 900, 1000, 1200, 1400, 1600, 1800, 2000$ atm. respectively $b_g = 918, 917, 914, 912, 912, 913, 919, 917, 917, 917, 917, 917$. From these values I concluded that $b_g = 917$.

After that the values of b (calculated) were determined as follows. We derive from equation (1):

$$\frac{b-b_0}{(v-b_0) - (b-b_0)} = 1 - \frac{(b-b_0)^2}{(b_g-b_0)^2}.$$

If we put $b-b_0 = y$, then we get for $b_g-b_0 = 454$:

$$\frac{y}{(v-b_0) - y} = 1 - \frac{y^2}{454^2},$$

from which follows:

$$y = 454 \sqrt{\frac{(v-b_0) - 2y}{(v-b_0) - y}}.$$

We know the values of y already in approximation from b (found). These values, substituted into the second member of the above equation, yield the accurate value of y , and so also of b .

III. Let us begin with assuming that the values of b_0 and b_g are independent of the temperature, which follows from the supposition of Prof. VAN DER WAALS, that the quantity α , which depends on the forces between the atoms, is proportional to the absolute temperature. Then we may calculate the *critical* quantities in the following way. Equation (1) in connection with the following equation:

$$v_k = \frac{3b_k}{1+2(\beta_1+\beta_2)} \text{ or } v_k - b_k = \frac{2}{3} v_k (1-\beta_1-\beta_2),$$

where

$$\beta_1 = \left(\frac{db}{dv} \right)_k; \quad \beta_2 = -\frac{1}{2} (v_k - b_k) \frac{\left(\frac{d^2b}{dv^2} \right)_k}{1 - \left(\frac{db}{dv} \right)_k},$$

yields after some reductions ¹⁾:

$$\frac{3}{2} \frac{1}{1+(1-x)\left(1+\frac{\mu}{\sqrt{x}}\right)} = \frac{1+\left(\frac{1-x}{1+x}\right)^3}{\left(1+\frac{(1-x)^2}{1+x}\right)^2}.$$

Here is $x = \left(\frac{b-b_0}{b_g-b_0}\right)^2$ and $\mu = \frac{b_0}{b_g-b_0}$. We may write for the second member:

$$\frac{2(1+3x^2)}{(1+x)(2-x+x^2)^2}.$$

Therefore we get also:

$$2-x+\mu \frac{1-x}{\sqrt{x}} = \frac{3(1+x)(2-x+x^2)^2}{4(1+3x^2)}. \quad . \quad . \quad . \quad (b)$$

The value of x may be derived from this equation. As $b_g=917=1,98b_0$, μ gets the value $\frac{1}{0,98}=1,02$, and we find in approximation for x the value 0,709.

Therefore

$$\frac{b_k-b_0}{b_g-b_0} = \sqrt{0,709} = 0,842,$$

from which we may easily derive:

$$\underline{b_k = 0,922 b_g = 845.}$$

Now we have:

$$\frac{3}{2} \frac{v_k-b_k}{v_k} = 1-\beta_1-\beta_2 = \frac{2(1+3x^2)}{(1+x)(2-x+x^2)^2} = 0,9163,$$

from which we find:

$$v_k = 2,57 b_k; \quad \beta_1 + \beta_2 = 0,0837.$$

The critical volume is therefore:

$$\underline{v_k = 2,57 b_k (= 2,37 b_g = 4,69 b_0) = 2172.}$$

At 0° C. this volume is (comp. the table) already reached at a pressure of about 700 atm. The values of r at 0° range in the experiments of AMAGAT to 1025; the verification of equation (1) of VAN DER WAALS may therefore be extended over volumes which have the size of liquid volumes; this fact compensates the want of experiments below the critical temperature.

We may also calculate the quantities β_1 and β_2 separately. From ²⁾

¹⁾ See v. D. WAALS, l. c. III, p. 652.

²⁾ VAN DER WAALS, l.c. III, p. 651.

$$\beta_1 = \frac{1}{1 + \frac{1+x}{(1-x)^2}} = \frac{(1-x)^2}{2-x+x^2}$$

follows:

$$\underline{\beta_1 = 0,0472; \quad \beta_2 = 0,0365.}$$

We find for RT_k : ¹⁾

$$RT_k = \frac{8}{27} \frac{a}{b_k} \frac{(1-\beta_1-\beta_2)^2(1+2(\beta_1+\beta_2))}{1-\beta_1},$$

or

$$RT_k = \frac{8}{27} \frac{a}{b_k} \times \frac{0,8396 \times 1,1674}{0,9528} = 1,029 \times \frac{8}{27} \frac{a}{b_k} = 0,305 \frac{a}{b_k}.$$

With $a = 300$, $b_k = 845$ we find therefore:

$$RT_k = 0,9994 \frac{T_k}{273} = 0,108,$$

which gives:

$$\underline{T_k = 29^\circ,5},$$

DEWAR found $T_k = 30^\circ$ à 32° ²⁾.

The critical pressure is represented by ³⁾

$$p_k = \frac{1}{27} \frac{a}{b_k^2} \frac{(1-\beta_1-4\beta_2)(1+2(\beta_1+\beta_2))^2}{1-\beta_1},$$

or

$$p_k = \frac{1}{27} \frac{a}{b_k^2} \times \frac{0,8068 \times 1,363}{0,9528} = 1,154 \times \frac{1}{27} \frac{a}{b_k^2} = 0,0427 \frac{a}{b_k^2}.$$

Introducing into this expression the values of a and b_k , we find:

$$\underline{p_k = 18,0 \text{ atm.}}$$

DEWAR found 15,4 atm.; OLZEWSKI ⁴⁾ 20 atm.

We find for the so called critical coefficient X : ⁵⁾

$$X = \left(\frac{pv}{RT} \right)_k = \frac{3}{8} \times \frac{1-\beta_1-4\beta_2}{(1-\beta_1-\beta_2)^2},$$

or

$$X = \frac{3}{8} \times \frac{0,8068}{0,8396} = \frac{3}{8} \times 0,961 = \underline{0,360}.$$

Finally the quantity V may be calculated from ⁶⁾

¹⁾ Id. II, p. 583.

²⁾ Proc. Royal Inst. **16** (2), N^o. 94 (1901), p. 477.

³⁾ v. D. WAALS, l. c. II, p. 583.

⁴⁾ Wied. Ann., **56**, p. 133 (1895). See also VERSCHAFFELT, These Proceedings, Febr., 1899, p. 327.

⁵⁾ v. D. WAALS, l. c. II, p. 584.

⁶⁾ Id. III, p. 648.

$$Y = \left(\frac{T}{p} \frac{dp}{dT} \right)_k = 4 \frac{1 - \beta_1 - \beta_2}{1 - \beta_1 - 4\beta_2} = 4 \times \frac{0,9163}{0,8068} = 4 \times 1,136 = \underline{4,545}.$$

Just as X comes again very close to the normal value 0,375, so Y for hydrogen approaches again close to the theoretical value 4. The expressions for T_k and p_k differ only little from those, found for these quantities for tri-atomic gases, such as CO_2 ; the expression for v_k on the other hand deviates strongly from it. This is to be ascribed to the fact, that b_g has here not the value of nearly four-times b_0 , but amounts to only twice that value. The quantities β_1 and β_2 are therefore much smaller than in the case of tri-atomic gases.

VAN DER WAALS found for CO_2 e.g. $\beta_1 = 0,138$ and $\beta_2 = 0,1$, the values we found above amounting to only about one third of these values. b_k is also in this case not 0,86 b_g but 0,92 b_g , and for v_k we find 2,57 b_k instead of 2,03 b_k , or 2,37 b_g instead of 1,75 b_g .

It is certainly of the highest importance to know whether the result for v_k agrees with the experiments. At the same time the value of the critical coefficient X will then agree, for the values of T_k and p_k agree very well. But with the investigation of this question, and with the verification of Y , we will wait till we have investigated the behaviour of b at higher temperature, which will be done in the next chapter.

IV. In the first place we will repeat the calculations of § 2 at 99°,25 C. We derive the following table (p. 581) from the experiments of AMAGAT¹⁾ at that temperature.

$v-b$ has here been calculated from

$$v-b = \frac{0,9994 (1 + 99,25 \times 0,0036627)}{p + \frac{a}{v^2}} = \frac{1,3627}{p + \frac{a}{v^2}}.$$

For the "calculated" values of b I determined quite in the same way as is indicated above for 0°:

$$\underline{b_g = 917} \quad ; \quad \underline{b_0 = 386}.$$

Again the initial values of b "found" (up to about 400 atm.) are too great. But afterwards the agreement is sufficient, though the verification was only possible up to 1000 atm., as, alas, no further experiments were available. We come to the remarkable result, that the value of b_0 has considerably decreased though the limiting value of b has remained unchanged. It seems that at higher temperature the atoms in the molecule may approach one another closer than at lower temperature.

¹⁾ l. c. p. 38 (2nd method).

100° C.

p	r	v^2	$\frac{a}{v^2}$	$v-b$	b found	b calculated from (1)	Δ
150	9846	96.94	3.0 ⁹	8902	944	902	+42
200	7567	57.26	5.2 ⁴	6640	927	897	+30
250	6200	38.44	7.8 ⁰	5286	914	892	+22
300	5286	27.94	10.7 ⁴	4385	901	887	+14
350	4636	21.49	13.9 ⁶	3744	892	881	+11
400	4147	17.20	17.4 ⁴	3265	882	876	+ 6
450	3766	14.18	21.1 ⁶	2892	874	871	+ 3
500	3462	11.99	25.0 ²	2596	866	866	± 0
550	3214	10.33	29.0 ⁴	2353	861	861	± 0
600	3006	9.036	33.2 ⁰	2152	854	856	- 2
650	2831	8.015	37.0	1983	848	851	- 3
700	2680	7.182	41.8	1837	843	846	- 3
750	2551	6.508	46.1	1712	839	841	- 2
800	2436	5.934	50.6	1602	834	836	- 2
850	2336	5.457	55.0	1506	830	831	- 1
900	2244	5.036	59.6	1420	824	827	- 3
950	(2174)	4.726	63.5	1345	(829) ¹⁾	822	—
1000	2093	4.381	68.5	1275	818	818	± 0

From equation (a) follows that for great volumes:

$$a(b_g - b_0)^2 = RT.$$

Now we find:

$$\begin{array}{l|l} 0^\circ & b_g - b_0 = 454 \quad (b_g - b_0)^2 = 20,61 \times 10^4 \\ 100^\circ & \text{,,} = 531 \quad \quad \quad = 28,20 \quad \text{,,} \end{array}$$

$(b_g - b_0)^2$ has therefore increased in the ratio 1:1,368. But T has increased in the ratio 1:1,364, from which would follow that a is independent of T .

In order to investigate whether this also applies to still higher temperatures, I have also performed the calculation for 200°, 25.

$v-b$ may then be calculated from:

$$v-b = \frac{0,9994(1+200,25 \times 0,0036627)}{p + \frac{a}{v^2}} = \frac{1,7324}{p + \frac{a}{v^2}}.$$

¹⁾ The value given for r at $p=950$ atm. appears to be erroneous; probably it must be 2164.

With the aid of the following table we may survey the results.

200° C.

p	v	v^2	$\frac{a}{v^2}$	$v-b$	b		Δ
					found	calculated	
150	12320	151.78	1.98	11399	921	894	+27
200	9420	88.74	3.38	8518	902	889	+13
250	7680	58.98	5.09	6791	889	884	+ 5
300	6520	42.51	7.06	5642	878	879	- 1
350	5694	32.42	9.25	4822	872	873	- 1
400	5075	25.76	11.65	4208	867	868	- 1
450	4593	21.10	14.22	3732	861	863	- 2
500	4210	17.72	16.93	3351	859	858	+ 1
550	3891	15.14	19.82	3040	851	853	- 2
600	3627	13.16	22.80	2782	845	848	- 3
650	3403	11.58	25.91	2563	840	843	- 3
700	3214	10.31	29.10	2376	835	838	- 3
750	3045	9.272	32.16	2214	831	833	- 2
800	2900	8.410	35.67	2073	827	828	- 1
850	2772	7.684	39.0	1949	823	823	± 0
900	2657	7.060	42.5	1838	819	819	± 0

Only at 150 and 200 atm. the values for b "found" are somewhat too high; furtheron the agreement is satisfactory. The experiments ranged only to 900 atm. The values of b "calculated" have been determined from (1) with the aid of:

$$\underline{b_g = 910}; \quad \underline{b_0 = 306}.$$

b_g appears to be slightly smaller than at 0° and 100°, but b_0 has again strongly decreased. It is a remarkable fact that the decrease of b_0 between 0° and 99° amounts to 77, and that between 99° and 200° to 80; so for each degree the same amount namely 0.8.

As to $b_g - b_0$; we have now:

$$\begin{array}{l|l|l} 0^\circ & b_g - b_0 = 454 & (b_g - b_0)^2 = 20,61 \\ 200^\circ & \text{,,} = 604 & \text{,,} = 36,48 \end{array}$$

The ratio of the values of $(b_g - b_0)^2$ is 1.77. For $1 + at$ we find 1.73. Taking for $b_g - b_0$ at 200° a value which is only 6 units

smaller, namely 598, the ratio of the values of $(b_g - b_0)^2$ would also have been found equal to 1,73. We may therefore safely assume that $(b_g - b)^2$ is found to be accurately *proportional* to the temperature within so large an interval of temperature as that between 0° and 200° , in consequence of which the quantity α must be *quite independent* of the temperature.

It is not astonishing that α is independent of the temperature; the contrary would rather seem to be remarkable. Being induced to make this contrary supposition for the better agreement of the

quantity $\frac{T}{p} \left(\frac{dp}{dT} \right)_k$ for CO_2 with the experiments, Prof. v. D. WAALS¹⁾ immediately pointed out its astonishing character.

We shall just draw attention to the following consequence of the fact, that $b_g - b_0$ is proportional to \sqrt{T} .

If we put:

$$b_g - b_0 = \sqrt{\gamma T},$$

then equation (1) may be written as follows:

$$\frac{b - b_g + \sqrt{\gamma T}}{v - b} = 1 - \frac{(b - b_g + \sqrt{\gamma T})^2}{\gamma T} = 2 \frac{b_g - b}{\sqrt{\gamma T}} - \frac{(b_g - b)^2}{\gamma T}.$$

With small value of $b_g - b$ and great value of v , we get approximately:

$$\frac{\sqrt{\gamma T}}{v} = 2 \frac{b_g - b}{\sqrt{\gamma T}},$$

therefore

$$b_g - b = \frac{\gamma T}{2v}.$$

v being in this case approximately equal to $\frac{RT}{p}$, we get:

$$b_g - b = \frac{\gamma}{2R} \cdot p,$$

or

$$\underline{b = b_g - \gamma' p},$$

i.e. the value of b depends only on p and no more on v or T , the value of b_g being nearly constant. The values of b , calculated for *the same* pressures, have therefore the same difference whether the temperature be 0° or 200° . For we have:

$$b_1 - b_2 = \gamma' (p_2 - p_1).$$

We found this fact affirmed in the above tables²⁾. For the purpose

¹⁾ l. c. III, p. 646.

²⁾ I pointed this out already before in a paper in the *Archives Teyler* („Sur l'influence des corrections, etc.” (2) VII, 3me partie, p. 26—27.) I tested there the b -values for hydrogen to an empirical formula of KAMERLINGH ONNES.

of a more direct comparison we collect the values of b for pressures differing each time 100 atm. in another table.

p	b		b		b	
	0°		100°		200°	
100	907	11	—	—	—	—
200	896	10	897	10	889	10
300	886	11	887	11	879	11
400	875	10	876	10	868	10
500	865	10	866	10	858	10
600	855	10	856	10	848	10
700	845	10	846	10	838	10
800	835	9	836	9	828	9
900	826	9	827	9	819	9
1000	817	—	818	—	—	—

We see that the differences are the same. All the values of b at 200° are 8 units less than the corresponding values at 0° and at 100°, because the value of b_g at 200° is 7 units less. But the course is always just the same. And as at a given value of p we always find *increasing* values of v at increasing temperature, so the value of b_0 must of course always decrease.

From the above follows also, that we may determine b_g immediately, e.g. adding 52 units to the values of b found at 500 atm., or 32 units to that at 400 atm., etc.

On the preceding reasoning we may base the following short calculation.

At $p_2 - p_1 = 100$ the initial value of $b_1 - b_2$ amounts to circa 10 à 11; we have therefore:

$$\gamma' = \frac{\gamma}{2R} = \frac{10,5 \times 10^{-6}}{100} = 0,105 \times 10^{-6}.$$

Therefore

$$b_g - b_0 = \sqrt{\gamma' T} = 10^{-3} \sqrt{0,21 RT} = 10^{-3} \sqrt{0,21 \times 0,9994 (1 + \alpha t)},$$

or

$$b_g - b_0 = 10^{-6} \sqrt{21 \times 10^4 (1 + \alpha t)}.$$

So we have at 0° $10^6(b_g - b_0) = 458$ (found 454).

At 100° we find $10^6(b_g - b_0) = \sqrt{21 \times 10^4 \times 1,3627} = 535$ (found 531).

At 200° we find $10^6(b_g - b_0) = \sqrt{21 \times 10^4 \times 1,7324} = 603$ (found 604).

V. A slight correction must of course be applied to the calculations of § 3 in consequence of the variability of $b_g - b_0$ with the temperature. For the assumption that b_g remains constant pleads also the circumstance, that according to an observation of D. BERTHELOT the experiment yields the value 2,93 à 2,98 for the ratio between the temperature at which a gas in extreme rarefaction follows the law of BOYLE, and the critical temperature; for which ratio the supposition that b_g is constant over this large temperature interval ¹⁾ leads to the value 2,9. If we assume this same supposition, we shall find b_g to be equal to circa 920 also for the critical isothermal. But b_0 will be found to be considerably higher than at 0°. We saw above that the difference amounts to 77 units for 99° difference in temperature. We shall therefore find b_0 at — 242° C. from the equation:

$$b_0 = 463 + \frac{242}{99} \times 77 = 463 + 188 = 651.$$

If therefore we put $b_g = 920$ and $b_0 = 650$, then in the first place b_g is no longer equal to $2 b_0$, but to:

$$b_g = 1,415 b_0.$$

The variability of b is therefore much smaller than at 0°, and in consequence of this the quantities β_1 and β_2 will also be found to be much smaller, and the critical quantities will approach still more closely to the normal values.

The quantity $\mu = \frac{b_0}{b_g - b_0}$ is here $\frac{1}{0,415} = 2,41$, and the value of $x = \left(\frac{b_k - b_0}{b_g - b_0} \right)^2$ of equation b ceases accordingly to be 0,709, but becomes 0,852. In consequence of this we find:

$$\frac{b_k - b_0}{b_g - b_0} = \sqrt{0,852} = 0,923,$$

from which follows:

$$b_k = 0,977 b_g = 899.$$

For v_k and for $\beta_1 + \beta_2$ we find (comp. § 3):

$$v_k = 2,87 b_k \quad ; \quad \beta_1 + \beta_2 = 0,0228.$$

So we find:

$$v_k = 2,87 b_k (= 2,80 b_g = 3,97 b_0) = 2579,$$

a volume which is reached at 0° C. at a pressure of ± 550 atm.

The values of β_1 and β_2 taken separately are:

$$\beta_1 = \frac{(1-x)^2}{2-x+x^2} = 0,0117 \quad ; \quad \beta_2 = 0,0111.$$

¹⁾ Zie VAN DER WAALS, l. c. III, p. 647.

Now we return to the experimental verification of v_k .

1 Gr. H_2 at 0° C. and 1 atm. occupying a space of 11127 cm^3 , v_k is expressed in cm^3 . equal to $2579 \times 10^{-6} \times 11127$, hence the critical *density* is:

$$d_k = \frac{1}{28,70} = \underline{0,0348}.$$

According to the theorem of the straight diameter of MATHIAS we have :

$$\frac{d_1 + d_2}{d_k} - 2 = \left(1 - \frac{T}{T_k}\right) \varphi,$$

which quantity φ has been found by YOUNG and MATHIAS to differ little from unity for different non-associating substances.

DEWAR¹⁾ found the density of the liquid phase at the melting point of H_2 ($16^\circ,5$) to be 0,086, so we find, neglecting the density d_2 of the vapour:

$$\frac{0,086}{d_k} - 2 = 1 - \frac{16,5}{31,0} = 0,468,$$

which yields for d_k :

$$d_k = \frac{0,086}{2,468} = \underline{0,0348},$$

in perfect agreement with the value of d_k we have calculated above.

We now proceed to the calculation of the other critical quantities T_k , p_k , X and Y .

We find for T_k :

$$RT_k = \frac{8}{27} \frac{a}{b_k} \times \frac{0,9549 \times 1,0456}{0,9883} = 1,010 \times \frac{8}{27} \frac{a}{b_k} = 0,299 \frac{a}{b_k}.$$

With $a = 300$, $b_k = 899$ we find therefore

$$0,9994 \frac{T_k}{273} = 0,100,$$

so

$$\underline{T_k = 27^\circ,2.}$$

This value is somewhat too low; the experiment has yielded $T_k = \pm 31^\circ$.

We find for the critical pressure:

$$p_k = \frac{1}{27} \frac{a}{b_k^2} \times \frac{0,9439 \times 1,093}{0,9883} = 1,044 \times \frac{1}{27} \frac{a}{b_k^2} = 0,0387 \frac{a}{b_k^2}.$$

¹⁾ I. c. bl. 477. DEWAR finds the melting point to be 16° à 17° ; the critical temperature to be 30° à 32° absolute temperature. [The density of the liquid phase at the boilingpoint (20° à 21°) has been estimated to be $\pm 0,07$, but then the vapour density may no more be neglected.]

With the values found for a and b_k we get:

$$\underline{p_k = 14,4 \text{ atm.}}$$

DEWAR found ± 15 atm.

The critical coefficient X becomes:

$$X = \frac{3}{8} \times \frac{0,9439}{0,9549} = \frac{3}{8} \times 0,989 = \underline{0,371},$$

so nearly the normal value 0,375.

For $Y = \left(\frac{T}{p} \frac{dp}{dT} \right)_k$ we find now another value than before. In the general expression ¹⁾

$$\frac{T}{p} \left(\frac{dp}{dT} \right)_v = 1 + \frac{1}{p} \left[\frac{a}{v^2} + \left\{ \left(\frac{dP_b}{db} \right)_t - T \frac{d^2 P_b}{dT db} \right\} \frac{db}{dv} \right]$$

the factor of $\frac{db}{dv}$ is now no longer zero. For as $\frac{dP_b}{db} = \alpha (b - b_0)$, we have:

$$T \frac{\partial}{\partial T} \left(\frac{dP_b}{db} \right) = -T \alpha \frac{db_0}{dT},$$

as we found α to be independent of T , b_0 on the other hand to depend upon T . We find therefore for the factor of $\frac{db}{dv}$:

$$\alpha \left(b - b_0 + T \frac{db_0}{dT} \right).$$

We have found above: $b_g - b_0 = \sqrt{\gamma T}$, so $b_0 = b_g - \sqrt{\gamma T}$, and as b_g has been found to be nearly independent of T , we get

$$T \frac{db_0}{dT} = -\frac{1}{2} \sqrt{\gamma T} = -\frac{1}{2} (b_g - b_0).$$

The factor of $\frac{db}{dv}$ becomes therefore:

$$\alpha \left(b - b_0 - \frac{1}{2} (b_g - b_0) \right),$$

and with

$$\alpha = \frac{RT}{(b_g - b_0)^2} = \frac{\left(p + \frac{a}{v^2} \right) (v - b)}{(b_g - b_0)^2} = \left(p + \frac{a}{v^2} \right) \left(\frac{v - b}{b - b_0} - 1 \right) \frac{1}{b - b_0}$$

— as according to (1) we have $\frac{1}{(b_g - b_0)^2} = \frac{1}{(b - b_0)^2} \left(1 - \frac{b - b_0}{v - b} \right)$ —

we get:

¹⁾ v. D. WAALS, l. c. III, p. 644.

$$\left(p + \frac{a}{v^2}\right) \left(\frac{v-b}{b-b_0} - 1\right) \left(1 - \frac{1}{2} \frac{b_g - b_0}{b - b_0}\right).$$

This expression for $\left(\frac{T}{p} \frac{dp}{dT}\right)_k$ becomes therefore, if we put $\frac{db}{dv} = \beta_1$:

$$\left(\frac{T}{p} \frac{dp}{dT}\right)_k = \left(1 + \frac{a}{p_k v_k^2}\right) \left[1 + \beta_1 \left(\frac{v_k - b_k}{b_k - b_0} - 1\right) \left(1 - \frac{1}{2} \frac{b_g - b_0}{b_k - b_0}\right)\right].$$

This yields with the values calculated above (see § 3):

$$Y = 4 \times \frac{0,9772}{0,9439} \left[1 + 0,0117 \left(\frac{1680}{249} - 1\right) \left(1 - \frac{1}{2} \cdot \frac{270}{249}\right)\right] = \\ = 4 \times 1,035 [1 + 0,0117 \times 5,747 \times 0,4578],$$

or

$$Y = 4,140 \times 1,0308 = \underline{4,267}.$$

Finally we investigate, whether this value of $\left(\frac{T}{p} \frac{dp}{dT}\right)_k$ may be brought into agreement with the few experimental data of DEWAR. DEWAR found namely (l.c.):

$$\begin{array}{l|l} T = 20^\circ \text{ à } 21^\circ & p = 1 \text{ atm.} \\ T_k = 30^\circ \text{ à } 32^\circ & p_k = 15 \text{ atm.} \end{array}$$

The two data yield by means of the integral formula

$$_{nep} \log \frac{p_k}{p} = f \left(\frac{T_k}{T} - 1 \right)$$

for f the value:

$$f = \frac{_{nep} \log \frac{15}{9}}{\frac{12}{20} \text{ à } \frac{9}{21}} = 2,708 \times \left(\frac{5}{3} \text{ à } \frac{7}{3} \right),$$

according as we take 20° and 32° or 21° and 30° . The lowest value is 4,51, so still higher than the calculated value 4,27. We must further note that 20° differs comparatively very much from T_k (being $\frac{2}{3} T_k$) and that therefore at 20° the factor f will certainly be found to be greater than near T_k , hence 4,51 is probably too great.

From the above we may in any case conclude, that the large extrapolation, by means of which we have calculated the value of b_0 at -242° from the values of b at 0° , 100° and 200° , really yields the critical data with a sufficient degree of accuracy — at least in so far as we may judge from the few data, that are available. Only Y is probably too low.

We have reason to expect à priori that the new equation, derived by VAN DER WAALS for the variability of b with the volume, does

not represent the experimental data with perfect accuracy. For the correction, introduced before for the partial coincidence of the distance spheres has not been taken into account in the deduction of this formula. The quantity b in $r - b$ for a monatomic gas, e. g. mercury vapour, argon etc. would according to the new theory of VAN DER WAALS remain invariable: whereas this quantity which according to the former considerations would for very large volumes be equal to four times the molecular volume, for smaller volumes would certainly have a smaller value, and it would approach to about twice the molecular volume — at least if the shape of the molecules does not exercise any influence on this calculation.

Physics. — *“Peculiarities and changes of Fraunhofer lines interpreted as consequences of anomalous dispersion of sunlight in the corona”* by Prof. W. H. JULIUS.

(Communicated in the meeting of February 28, 1903).

Especially by JEWELL's investigations on the coincidence of solar and metallic lines¹⁾ attention has been drawn to several variable peculiarities of Fraunhofer lines. Here we do not mean the irregularities occurring in the spectrum of spots or of faculae, which relate to disturbances in comparatively small parts of the sun, but abnormalities shown by the average sunlight, as observed when the slit is illuminated by a long strip of an imperfectly focused solar image. In that case, according to DOPPLER's principle we may, of course, expect displacements of the lines in consequence of the Sun's rotation, of the rotation of the Earth, and of the change in the distance between Sun and Earth caused by the excentricity of the Earth's orbit. But even when all these influences have been allowed for, some irregularities still remain.

Indeed, JEWELL has observed that some Fraunhofer lines do, others do not, exactly coincide with the emission lines in the arc spectrum of elements, and that the displacements are unequal both for lines of different elements and for the various lines of one and the same element. Moreover, the shifting of certain lines on one set of photographic plates was sometimes found different from that on a set of

¹⁾ L. E. JEWELL, “The coincidence of solar and metallic lines. A study of the appearance of lines in the spectra of the electric arc and the Sun.” *Astroph. Journ.* III p. 89—113, 1896. The same: “Spectroscopic notes. Absolute wave-lengths, spectroscopic determinations of motions in the line of sight, and other related subjects.” *Astroph. Journ.* XI p. 234—240, 1900.

plates taken at another time. With several lines the intensity too appeared to be variable.

JEWELL explains these phenomena on certain hypotheses on density, pressure and temperature of the absorbing and emitting gases in the different layers of the solar atmosphere, and by variable ascending and descending velocities of matter.

HALE'S *abnormal solar spectrum*.

Much greater than the irregularities mentioned are those, found in an "abnormal" solar spectrum, lately described by G. E. HALE.¹⁾

This highly remarkable spectrum had accidentally been photographed as long ago as February 1894 in a series of exposures made with the sole intention of investigating the peculiarities of the grating. Only a few months later it was discovered that a very extraordinary phenomenon had been photographed. HALE hesitated to publish this accidental discovery. Copies of the plate were sent to several spectroscopists for examination with the request that an explanation, referring the phenomenon to some origin other than solar, might be supplied, if possible. As no such explanation was forthcoming, the spectra were very carefully measured and described.

On one and the same plate 12 exposures had been successively made in the third order spectrum of a plane grating. A solar image of 51 m.m. in diameter was so adjusted that the image of a spot fell exactly on the slit. The length of the slit (6.5 m.m.) corresponded to about one eighth of the sun's diameter.

The first exposures show the normal spectrum without any considerable changes. Then came the disturbance, which culminated in the eighth spectrum and, in the following four, decreased rapidly. HALE gives reproductions of four spectra, each of them extending from 23812 to 24132. N°. 1 has been taken before the disturbance occurred; N°. 2 is the most abnormal spectrum; N°. 3 is called by HALE the "intermediate" spectrum, it has been obtained a few moments after the abnormal one; N°. 4 shows once more the normal solar spectrum, as it was photographed at another time on another plate. Nos. 1, 2 and 3 show a dark band throughout the whole spectrum, corresponding to the sun-spot which had been focused on the slit.

The most prominent features of the abnormal spectrum are :

1°. The band due to the spot appears much fainter than in the spectra, photographed before and after the disturbance.

¹⁾ GEORGE E. HALE. "Solar research at the Yerkes Observatory". *Astroph. Journ.* XVI p. 211—233, 1902.

2°. With several Fraunhofer lines the intensity or the width is greatly diminished. This is most conspicuous with the broad, dark calcium bands H and K and with the hydrogen line H δ , these being almost totally absent in the abnormal spectrum.

3°. Other lines, on the contrary, appear uncommonly strengthened.

4°. Many lines are more or less displaced.

The same peculiarities are noticed, though generally in a smaller degree, in the intermediate spectrum, so that the latter, in fact, forms a link between the abnormal and the normal spectrum.

This marvellously complicated disturbance was not confined to light coming from a comparatively small part of the solar disk, for instance from the immediate surroundings of a spot; on the contrary, it extended almost equally over the whole width of the spectrum and was therefore nearly the same for all the light which came from a very great area of the Sun.

The moments of the 12 exposures and the exact date had not been recorded, but there was sufficient evidence that the whole process of the disturbance lasted only a very short time.

HALE calls the phenomenon: "a remarkable disturbance of the reversing layer". But is it not almost impossible to imagine a rather thin layer in the solar atmosphere undergoing suddenly and simultaneously over a great part of the sun such a thorough change, as to make its absorbing and radiating power in some parts of the spectrum for a while nearly unrecognizable?

It occurred to me, therefore, that the origin of the phenomenon should be looked for somewhere on the path of the light between the Sun and the Earth. If on this path there be media, causing anomalous dispersion, the beam must show an altered composition.

As I formerly indicated ¹⁾, the properties of the chromospheric light may be derived from the supposition, that this light has been scattered out of the photospheric light by anomalous dispersion. According to this hypothesis the spectrum of the chromosphere informs us, which are the kinds of light, that may follow rather strongly curved paths in the solar atmosphere. So the idea suggested itself, that the same waves might play a striking part in HALE's abnormal spectrum.

In order to investigate the question as impartially as possible, I marked (before consulting HALE's table or a table of chromosphere

¹⁾ Proc. Roy. Acad. Amst. II, p. 575—588; III, p. 195—203; IV, p. 162—171; Physikalische Zeitschrift 4, p. 132—'36.

TABLE I.

Lines whose intensity is less in the abnormal than in the normal spectrum.

Wavelength	Intensity				Elements	Remarks.
	normal (ROWLAND)	inter- mediate (HALE)	abnormal (HALE)	Chromo- sphere (LOCKYER)		
3871.4				4	C	Not mentioned in HALE's list, but distinctly weakened in the abnormal spectrum on the reproduction.
3872.6				4	Fe	
3874.09	4	9	—	2 (?)	Fe	
3878.47	22	25	—	3 3	Fe, Fe	
3889.05	?	15	—	8	H	
3895.80	7	12	—	3	Fe	λ = 3878.15 and λ = 3878.72; HALE mentions Fe, Mn.
3899.30	5	4	—	2	V?	
3903.09	10	12	—	2—3	Fe	
3905.66	12	20	—	2	Cr, Si	
3906.70	14	—	4	2	Fe	
3913.63	9	7	—	6	Ti	
3914.49	7	8	5*		Ti	* These intensities are very probably estimated too high when compared with the numbers in the second column. Cf. the Note on p. 593.
3916.54	3	—	4*	3	V	
3920.41	10	10*	10*	3	Fe	
3923.05	12	12*	12*	3	Fe	
3933.82				10	Ca	
3944.16	15	15*	12*	5	Al	
3948.91	13	15	—	3	Fe	
3950.10	5	—	2	3	Fe	
3953.02	17	15	—		Fe, etc.	
3958.35	5	8	—	4	Ti	
3961.67	20	20	—	6	Al	
H 3968.63	(700)	7	7	10	Ca	
H _e 3970.18	7	8	—	10	H	
3977.89	6	8	—	2	Fe	
3986.90	6	8	—			
3998.78	4	4	4*	4	T	
4012.50	5	4	5*	5—6	Ti, etc.	
4033.22	7	12	3	3—4	Mn, Fe	
4034.64	6	10	—	3—4	Mn, Fe	
4045.98	30	30	5	7	Fe	
4063.76	20	20	—	6—7	Fe	
4071.91	15	15	15*	6	Fe	
4077.88	8	10	7*	10	Sr	
H 4102.00	40	7	—	10	H	

lines) on the reproductions of the spectra in the *Astrophysical Journal* a number of lines, which struck me as being weakened in the abnormal spectrum. By means of GEORGE HIGGS' photographic atlas of the normal solar spectrum the wave-lengths of the selected lines were easily read; they are to be found in the first column of Table I.

The second, third, and fourth columns show the intensities of these lines in the normal, the intermediate, and the abnormal spectrum as given by HALE (for the normal spectrum from ROWLAND's tables, for the other two from estimations by Mr. ADAMS). HALE remarks that the intensities of the lines were estimated independently for the two disturbed spectra¹⁾. The fifth column indicates the intensities of corresponding chromosphere lines as found by LOCKYER in

TABLE II.

Lines whose intensity is greater in the abnormal than in the normal spectrum.

Wave-length	Intensity.				Elements.	Remarks.
	normal	intermediate	abnormal	Chromosphere		
	(ROWLAND)	(HALE)	(HALE)	(LOCKYER)		
3921.86	4	—	20		Zr, Mn	
3927.77	—	—	25		?	
3930.45	8	15	28	3-4	Fe	
3937.39	—	—	40		?	
3940.25	—	7	42		?	
3950.50	2	—	43		Y	
3962.29	3	—	41		Fe?	
3973.77	6	—	45	2?	Ni, Zr, Fe, Ca	
3981.92	4	13	30	6*	Ti, Fe	* In HUMPHREYS' table of chromosphere lines (1901 eclipse) this line does <i>not</i> occur.
3992.97	3	4	40		V, Cr.	
3996.80	—	—	9		?	
4013.90	8	42	45		Ti, Fe	
4014.67	5	9	20		Fe	
4023.38	—	—	40		?	
4033.77	2	3	45		Mn	
4040.79	3	6	20	4	Fe	
4044.09	5	20	45		Fe	

¹⁾ In selecting the lines that appeared weakened in the abnormal spectrum I did of course compare the three spectra mutually. That is why in my table some lines occur, whose intensities, as estimated by Mr. ADAMS, are not comparatively low in the abnormal spectrum.

the spectrum, secured at Viziadrug during the 1898 eclipse¹); the sixth column shows the absorbing substances.

In a similar way Table II has been composed; here we find the lines, which on the reproduction appeared to be strengthened in the abnormal spectrum.

The result is very striking. Weakened lines correspond to chromosphere lines, almost without exception; most of the strengthened lines, on the other hand, are not to be found in the spectrum of the chromosphere.

LOCKYER gives the strength of the chromosphere lines on a scale such that 10 indicates the strongest and 1 the faintest lines. If we take into account that in his list the greater part of the lines bear the numbers 1 and 2, our table shows us, that by merely observing the abnormal solar spectrum we have been able to pick out strong chromosphere lines. This cannot be chance. Undoubtedly both phenomena — the weakening of Fraunhofer lines in the abnormal spectrum and the origin of the chromosphere spectrum — are to be explained in close relation with each other.

The strengthening of lines in the abnormal spectrum does not, on the contrary, seem to be so directly connected with the composition of the chromosphere spectrum.

If our view be correct that the chromospheric light has been separated by strong ray-curving from the "white" light emitted by deeper layers, those special radiations must, as a rule, show reduced intensity in the spectrum of the Sun's disk²). Fraunhofer lines cor-

¹) LOCKYER, CHRISHOLM-BATTEN and PEDLER. "Total Eclipse of the Sun, January 22, 1898. — Observations at Viziadrug," Phil. Trans., A, vol. 197, p. 151—227, 1901.

²) It might be thought that the rays forming the chromosphere light, need to be absent only from the spectrum of the edge but not from that of the central portions of the Sun's disk. By a simple consideration, following from a look at Fig. 4 of my paper, read in Febr. 1900 (Proc. Roy. Acad. Amst. II, p. 580) we see, however, that the chromosphere light visible to us may very well, for a part, have its origin even in points of the Sun which lie opposite to the Earth's direction. The chromosphere light, reaching the Earth, may proceed from any point of SCHMIDT's "critical sphere". For the greater part it is likely to come from the back half of the Sun. But then the half, facing us, furnishes the chromospheric light which travels to other regions of the universe, and this light, of course, is wanting in the spectrum of the disk. (There is some reason for supposing that, on an average, more chromospheric light is sent forth in directions making great angles with the Sun's equator, than to the equatorial regions, including the Earth's orbit.)

responding to chromosphere lines will therefore have a more or less darkened background in the ordinary solar spectrum. The rate of darkening at various distances from the centre of an absorption line is, of course, connected with the shape of the dispersion curve near that line; whereas the average shading depends 1st on the quantity of matter causing anomalous dispersion and 2^{ndly} on the slopes and the directions of the density gradients in the gases through which the light is transmitted, viz. on the Sun's "activity" ¹⁾).

We distinguish, therefore, a twofold origin of the dark lines in the solar spectrum: real absorption of those waves, exactly corresponding to the periods of the media, and dispersion of the strongly deviated neighbouring light ²⁾).

The dispersion will be especially evident where extraordinary differences in the density of the medium occur; in this way the widening of most of the Fraunhofer lines in the spectra of spots may be accounted for.

Dispersed light has not, of course, vanished; the absence of certain rays in the spectrum of a spot is counterbalanced by the increased intensity of the same radiations in the light coming from the neighbouring faculae. Thus the distribution of the density in the solar gases may locally be such, that a limited part of the disk seems to emit a considerable amount of rays with abnormally high or abnormally low refractive indices. In the spectrum of such parts not only will the Fraunhofer lines show narrower and fainter than usually, but here we may even meet with lines contrasting brightly with their surroundings. These bright lines will not coincide with the corresponding absorption lines; their average wave-length will in general be greater or smaller than that of the absorbed light, for, according to the accidental distribution of the density, we shall find either the rays with high or those with low refractive indices most prominent in the beam.

The above considerations suggest an explanation of HALE's abnormal spectrum.

In fact, the lines showing especially faint in this spectrum were exactly those, causing strong anomalous dispersion — witness the

¹⁾ The possible influence of the general or regular ray-curving (after SCHMIDT's principle) on the feature of the spectral lines has, in the present paper, been left out of consideration. If we were able to observe or to calculate the radii of the "critical spheres" for radiations undergoing anomalous refraction, it would be possible to estimate that influence; but as yet sufficient data are wanting.

²⁾ Proc. Roy. Acad. Amst. II, p. 580.

chromosphere spectrum. With H , K , H_2 and some iron lines it is conspicuous that the abnormal faintness regards mainly the broad dark shadings of the lines, i. e. those parts, whose darkness in the normal spectrum we attributed not to absorption, but to dispersion. Moreover, the dark band due to the spot has nearly disappeared. This means that waves, which in normal circumstances are wanting in the spot spectrum on account of their strong dispersion, at the time of the disturbance had been gathered again into the beam reaching the instrument.

How all this may happen will become evident as soon as we shall be able to establish a plausible cause, by which, within an angular space great enough to include a considerable part of the solar disk, the strongly dispersed rays might be gathered again.

It is not necessary to introduce a new hypothesis for the purpose. The same idea about the Sun's constitution¹⁾ which enabled us to explain the properties of the chromosphere and the prominences, furnishes us once more with the required data.

Indeed, if (according to SCHMIDT's theory) the Sun is an unlimited mass of gas, surfaces of discontinuity must exist similar to those, whose general feature has been determined by EMDEN²⁾ for a sharply outlined radiating and rotating sun. These surfaces must extend unto the remotest parts of the gaseous body — a conclusion in excellent harmony with the visible structure of the corona. For along the surfaces of discontinuity waves and whirls are formed; the core-lines of the vortices nearly coincide with the generatrices of these surfaces of revolution, and in these cores the density is a minimum. This may account for the streaky appearance, shown more or less distinctly in all good photographs and drawings of the corona.

This particular appearance may have another cause, though; for what follows, however, this is immaterial. We only assume that the density of the coronal matter varies in such a way, as to correspond to the striped structure visible at the time of a total eclipse of the Sun.

A coronal streamer which, at a given moment, runs exactly in the direction of the Earth may be very roughly compared, then, to a bundle of glass tubes through which we are looking lengthwise. Such a structure will gather and conduct rays of various directions, entering it at one end. This takes place also if the parts with the greater and those with the smaller optical density do not alternate abruptly, like glass and air, but gradually.

¹⁾ Proc. Roy. Acad. Amst. IV, p. 162.

²⁾ R. EMDEN, Beiträge zur Sonnentheorie, Ann. d. Phys. [4], 7, p. 176—197.



Fig. 1.

In Fig. 1 the optical density of the matter may be represented by the compactness of the streaking. A ray for which the medium has a large positive refraction constant would for instance follow the path AA' , curving round the denser parts of the structure; a ray BB' , for which the medium possesses a large negative refraction constant, would move in a similar way through the more rarefied regions. On the other hand, the light CC' for which the constant exactly equals zero is not influenced by the fluctuations of the density; and if for some kind of light the refraction constant is very nearly zero, the ray would have to travel a long way almost parallel to the structure before its curving would be perceptible.

Now the corona sometimes shows exceedingly long, pointed streamers. We only have to suppose that the Earth was exactly in the direction of such a streamer at the moment the abnormal spectrum was photographed; then all the irregularities observed in this spectrum become clear. Light, under normal circumstances absent from the solar spectrum through strong dispersion, has been collected by the coronal streamer; hence the weakening of the Fraunhofer lines, especially also of those in the spectrum of the spot. As the abnormalities were caused by a peculiar distribution of matter in the vast regions of the corona, lying between the source of light and the Earth (and not by disturbances in a relatively thin "reversing layer") they could appear in the same way over a great part of the Sun's disk. The rarity of the phenomenon is the result of the slight chance we have to take a photograph at the very moment on which an uncommonly long coronal streamer is projected exactly on the part of Sun's disk illuminating the slit; the short duration finally is a consequence of the difference between the angular velocity of the corona and that of the Earth in its orbit.

As we have mentioned before, *no* chromosphere lines correspond, in general, to those lines showing extraordinarily *strong* in the abnormal spectrum. How are we to account for the strengthening of these lines?

We might be tempted to think of absorption in the corona; for if it be true that a streamer was turned towards the Earth, the rays had to go an uncommonly long way through an absorbing medium. But on closer examination this idea is less probable.

The particles of the extremely rarefied corona gases will hardly influence each other; their periods will, therefore, be almost absolutely constant, so as to cause very sharp, narrow absorption lines. Thus it is difficult to understand, how an absorption line, already present in the normal solar spectrum, might be strengthened by the absorbing power of the corona. Further, in studying HALE's table, we observe that many lines which are strong in the abnormal spectrum, show a much smaller intensity in the intermediate spectrum (taken only a few moments later); whilst the reverse happens as well, viz. that lines are strong in the intermediate and very weak in the abnormal spectrum. This hardly fits in with the absorption hypothesis. Some lines showing this peculiarity are given in table III.

TABLE III.

Lines whose intensity is very different in the intermediate and the abnormal spectrum.

Wave-length	Intensity.				Elements	Remarks.
	normal (ROWLAND)	inter- mediate (HALE)	abnormal (HALE)	chromo- sphere (LOCKYER)		
3905.66	12	20	—	2	<i>Cr, Si</i>	
3905.81	21	—	20		<i>Si</i>	
3921.71	9	14	—		<i>Ti, La, Zr, Mn</i>	
3921.87	4	—	20		<i>Zr, Mn</i>	
3950.33	—	10	—		?	
3950.51	2	—	13		<i>Y</i>	
3972.30	2	12	—		<i>Ni</i>	
3972.64	2	—	12		?	
4005.86	3	25	5		?	
4057.39	4	—	15	1—2	<i>Co, Fe</i>	
4057.66	7	10	—		?	

In the chromosphere spectrum corresponding lines seem to be wanting. (At λ 3905.66 and λ 4057.39 the faint chromosphere line may possibly belong to another element than the abnormally strengthened absorption line).

To arrive at a more satisfactory explanation of the strengthening-phenomenon we suppose that these absorption lines do indeed cause anomalous dispersion of neighbouring waves, but in a very slight

degree. Then, the refractive indices of the neighbouring waves differing hardly from unity, the direction of those rays will only be perceptibly changed after they have travelled a very long way through the corona and almost parallel to its structure-lines. Whereas the strongly refracted rays, entering the coronal streamer in various directions, were obliged to follow the structure-lines, curving about them, and so in a sense were concentrated on the Earth, it may happen with the extremely slightly curved rays we are now considering, that they have been bent for instance only once over the whole length of the streamer and continue their way in a direction not meeting the observing station. The divergence of a beam consisting of these rays will have increased, the intensity diminished. Thus, the resultant spreading of neighbouring light causes the absorption line to appear somewhat widened and therefore strengthened. But obviously it must be possible too, that, after a short time, under the influence of another part of the corona, circumstances turn out even favourable for that slightly curved light to reach the observer. In that case the absorption line is weak again. (Similar alternations, of course, also occur with the more strongly refracted rays, and that in quicker succession, but this does not alter the fact of their *average* intensity appearing increased as long as the structure lines of the coronal streamer are turned towards the spectroscope. For a detailed discussion of this case see the Note at the end of this paper).

In both abnormal spectra a number of absorption lines are more or less displaced. Perhaps this is partly due to motion in the line of sight; but after the foregoing it will not be necessary to explain in detail, that also anomalous dispersion can account for this phenomenon. Dissymmetric form of the dispersion-curve as well as a peculiar distribution of the density of the coronal matter may unequally affect the intensity of the light on both sides of the absorption line, and thus bring about a seeming displacement of the line.

Certain peculiarities of lines in the normal solar spectrum.

If we have been right in connecting the uncommonly great abnormalities in HALLE'S spectrum with a very particular position of the Earth with respect to the corona, it is to be expected that similar irregularities, though to a smaller degree, will ever be found, as the sunlight always reaches us through the corona.

According to JEWELL'S above mentioned investigations this supposition proves to be well founded. Many solar lines have varying intensities and positions, so that JEWELL deems them unfit for standards for

very accurate determinations of wavelengths. And these are for the greater part the most prominent lines of the spectrum, especially the shaded ones ¹⁾.

JEWELL emphasizes the fact that all distinctly shaded lines in the solar spectrum show to a greater or less degree the following typical feature ²⁾.

Within a broad, shaded, moderately dark background a much darker central absorption line contrasts rather sharply (Fig. 2).



Fig. 2



Fig. 3.

Besides, the absorption curve often shows dippings close to the central line, as in Fig. 3, sometimes symmetrical, sometimes dissymmetrical. JEWELL affirms that this is not an optical delusion, due to contrast, but a real phenomenon. He assumes, therefore, that the broad absorption band is produced in the lower portions of the solar atmosphere and under a great range of pressure; that in higher levels radiation prevails again, producing a rather wide emission line; and that finally in the highest parts, where the pressure is very much less, the sharp absorption line is produced. The position of this central absorption line with respect to the emission line is usually unsymmetrical, which is conspicuous in the case of *H* and *K*. The central line itself also varies somewhat in width upon different plates and its maximum of intensity is not always in the middle of the line. The displacement of this central line in *H* and *K* varies in magnitude, but, so far as has been observed, always toward the red with respect to the emission line and the corresponding metallic line (in the arc).

JEWELL concludes that the absorbing calcium vapour descends all over the solar surface with a velocity sometimes amounting to about 75 miles per minute.

Upon the same plates showing strong dissymmetry in *H* and *K*, the shaded lines of other elements (*Fe*, *Al*, *Mg*, *Si*) have been examined. The strongest iron lines and one aluminium line showed displacements of the same character as that observed in the case of

¹⁾ *Astroph. Journ.* XI, p. 236, 1900.

²⁾ JEWELL, "Certain peculiarities in the appearance of lines in the solar spectrum and their interpretation". *Astroph. Journ.* III, p. 99, 1896.

H and *K*, but to a much smaller degree and sometimes toward the violet, sometimes toward the red. Certain shaded lines of *Mg* and *Si*, on the contrary, showed no evidence of a displacement, nor did the iron lines without considerable shading, the faint calcium line at λ 3949,056 and many other lines.

If we admit no other explanation of line-shifting and -widening besides those, based on DOPPLER's principle and on the effect of pressure and temperature, we arrive at very strange conclusions relative to the condition of the elements in the solar atmosphere. Not less surprising is, as noticed by JEWELL¹), the small amount of the absorption in the shaded parts of the lines, when we consider the enormous depth of the solar atmosphere and the high pressure which must exist in the absorbing layers, for them to produce a broad absorptionband.

By making various suppositions concerning the condition of the gases in the solar atmosphere, JEWELL succeeds in finding an interpretation of most of these astonishing facts. But it must be granted that his explanations include a greater number of arbitrary and mutually independent hypotheses than is the case with our explanations, founded as they are on selective ray-curving and readily deduced from that principle for each separate phenomenon, without introducing new suppositions.

Only the dark central lines of the Fraunhofer lines are to be ascribed, in our theory, to real absorption. Their shaded background of varying intensity we consider as an effect of anomalous dispersion of the not absorbed neighbouring waves. This selective scattering will be strongest in those places where the density-gradients are relatively steep, viz. in whirls in the deeper regions of the gaseous body. But some of the widely dispersed rays may be gathered by the corona owing to its "tubular" structure and be conducted along its greater or smaller streamers.

This will especially apply to the most strongly refracted waves, whose position in the spectrum is very close to the real absorption lines; thus pseudo emission lines are produced in about the middle of the pseudo absorption bands.²)

¹, *Astroph. Journ.* III, p. 106.

²) A most remarkable fact is that the shading of *K*, *H*, the iron-line λ 3720,086 and of some other strong shaded lines is sometimes partially broken up into a series of faint nebulous lines, symmetrically situated about the central line. In each case the distance apart of the component lines increased as the distance from the center increased (JEWELL, *Astrophysical Journal* 8, p. 51—53).

It might have been predicted by our theory that we should meet with this phenomenon now and then.

Most likely HALE's abnormal spectrum has shown us a case, where these seeming emissionbands acquired an uncommon extent. We may therefore expect that a systematical investigation of solar spectra, photographed at different times, will afford all kinds of intermediate cases.

It would be desirable, for the moments when the photographs are taken, to know form and position of the coronal streamers extending toward the Earth. At all events the actual phase of the sun-spot period, with which the shape of the corona seems to be connected, should be taken into consideration; and perhaps the simultaneous observation of the photospheric reticulation, discovered by JANSSEN, may procure some evidence concerning the position of coronal streamers, and thus contribute to our knowledge of their influence on the Fraunhofer spectrum.

Mineralogy. — "*On the refractive index of rock-glasses,*" by P. TESCH :
(Communicated by Prof. J. L. C. SCHROEDER VAN DER KOLK).

Of the group of the igneous rocks, the origin of which out of fluid red-hot condition we accept, the volcanic rocks constitute that subdivision, which includes the rocks, that as lavas have broken through the surface of the earth.

The quick cooling at the atmosphere renders it possible that in these rocks part of the magma congeals amorphously, so that next to the minerals a rockglass appears, which constitutes either an inferior part or a prevailing one of the rocks. So in general this glass

Let us consider a beam of light of an exactly defined wavelength belonging to the shaded background of an absorption line. This beam leaves the deeper layers of the Sun with a certain divergence. As it passes along a "tube" of the corona, its divergence will alternately diminish and increase, and on reaching the Earth it shows in the spectrum an intensity, depending on the divergence (or perhaps convergence) with which it has left the last traces of the corona. For a beam of light whose wavelength is only slightly nearer to that of the absorption line, the medium will have a considerably greater refraction constant, so that the rays of this beam, on their way through the corona, may make part of a bend more than the former ones. The beam may therefore arrive with a quite different degree of divergence and, consequently, of intensity. Thus, proceeding towards the absorption line from either side, we easily see that we must meet with a periodically changing intensity. Rays, corresponding to the middle of one of the so formed fringes, will have made one full bend more or less than the rays, belonging to the middle of the next fringe.

If this interpretation be correct, the width and the number of fringes visible must prove to be variable. As far as I know, the observations made on this point are not numerous. May the proposed views serve to further the investigation of this interesting phenomenon.

consists of silica and metal-oxides. We may suppose that the silica, which is most likely to be the principal part, will also have a prevalent influence on the physical characters of such natural glass.

A determination of the specific gravity of the glass is made more difficult by the presence of many gas-bubbles. If this obstacle did not exist, the specific weight would be a better expedient for a quick temporary orientation than the determination of the refractive index, for which more instruments are necessary. With respect to the specific gravity it could be stated, that with these rocks where the value of the index the use of bromoform as liquid of comparison necessitated and whose exponent proved to be greater than that of bromoform (1,593), the specific gravity of the glass was still higher than that of bromoform (2,88). The small air-free, not to be isolated grains, still sank in this liquid. Now I have tried to find out in how far the refractive index is dependent on the SiO_2 percentage. For that purpose 16 rocks have been examined, forming a series of the most acid to the most basic magmas, which occur in nature.

The result has been comprised in the following table:

Name	Origin	SiO_2	Index
Granite	Magurka, Hungary	72,65	1,500
Granite	Brocken, Harz Mountains	71,19	1,500
Granite	Auvergne	70,62	1,500
Granite	Korinitzsch, Hungary	67,31	1,510
Quartzdiorite	Adamello, Tyrol	66,58	1,510
Syenite	Plauensche Grund, Dresden	60,26	1,520
Elacolite-syenite	Ditro,	59,88	1,525
Diorite	Hodritsch, Hungary	59,57	1,525
Syenite	Ditro,	57,36	1,530
Augite-syenite	Monzoni, Tyrol	53,75	1,550
Chrysolitenorite	Radau Valley, Harz Mountains	53,64	1,550
Diorite	Auvergne	50,86	1,570
Quartzdiorite	Dumkuhlen Valley, Harz	48,89	1,585
Basalt	Dyrafjord, Iceland	48,50	1,590
Gabbro	Radau Valley, Harz	44,08	1,620
Harzburgite	Harzburg, Harz	42,24	1,630

From this we see that a classification exclusively according to decreasing SiO_2 percentage, coincides with an increasing value of the refractive index.

Apparently the metal oxides present have only little influence on that value, at least this influence falls within the limits of the errors of observation.

A chrysolite-norite and an augite syenite with about the same SiO_2 percentage have also the same index, whereas the oxides, especially MgO are sure to be there in quite another relation, for in the chrysolite-norite the minerals containing Mg come strongly to the foreground.

As regards the colour of the glass it will be almost wholly dependent on the iron-percentage.

With the examined glasses the colour changed from light green to dark brown. Just as with isomorphous mineral series, as e. g. the enstatite-hypersteneseries, the dark colour most likely points to a greater iron percentage than the light one.

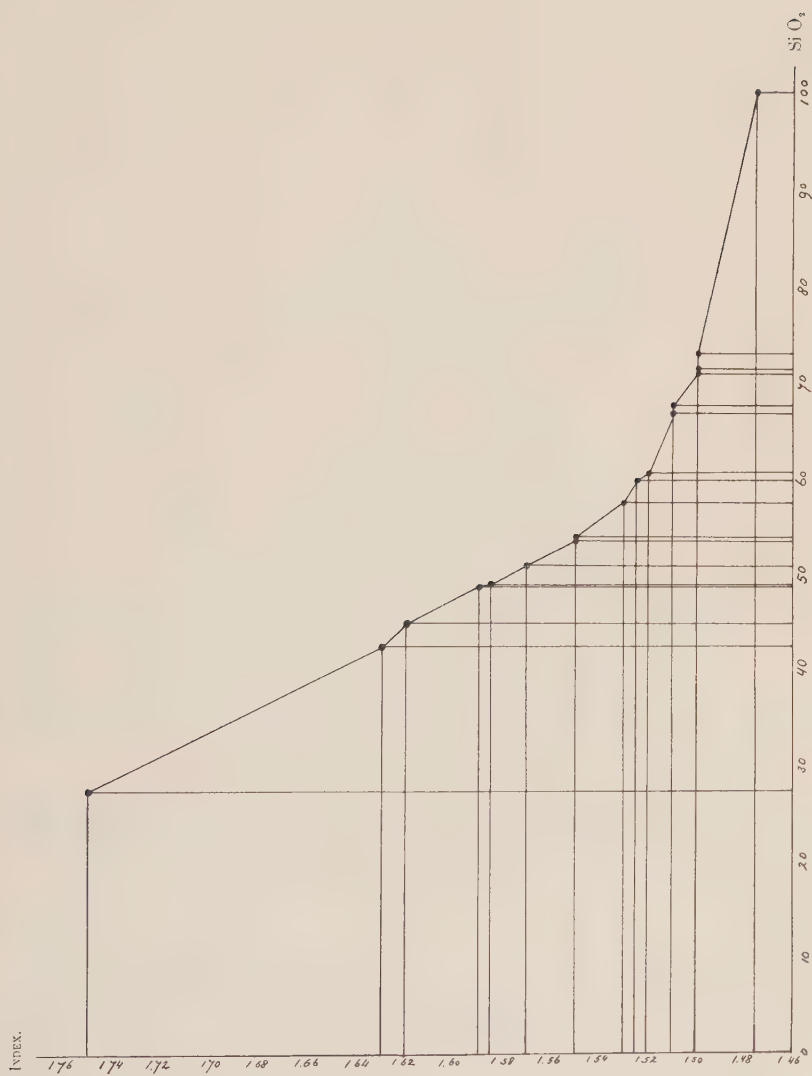
The typical amorphous glassfracture can be easily distinguished at the splinters under the microscope.

The fusion of the rock-powder took place in a gasflame in which compressed oxygen was blown. As an underlayer a cupel of chalk or bone-ash was used. But care has to be taken that the melted magma of the cupel remains isolated, because there is a chance that oxides of alcaleic earths will be absorbed by the cupel and in consequence the composition of the magma does not answer any more to that of the rock. This can be obtained by directing the point of the flame towards the middle; the upperlayer then fuses quickly to a little ball, which remains isolated by the underlaying rock-powder of the cupel. To control the regularity found in the independence of the refractive index of the SiO_2 percentage, two mixtures of the following composition were made:

	I.	II.
SiO_2	60 %	60 %
Fe_2O_3	10	20
Al_2O_3	10	5
CaO	10	5
MgO	5	10
$\text{K}_2\text{O}, \text{Na}_2\text{O}$	5	—

Of both the mixtures the fused glass had the index 1.520; here we see again the prevalent influence of SiO_2 .

At last some slags and melted minerals were investigated.



Composition.	Index.
SiO ₂ 45,5	1,600
CaO 19,8	
FeO 5,3	
SiO ₂ 27,4	1,750
FeO 41,7	
CuBi 0,2	
Pb 1,5	
Al ₂ O ₃ 0,8	
ZnO 21,8	
MnO	

In this slag the ZnO plays the part of the MgO. When ZnO is replaced by MgO, the index remains the same.

Finally the index of the following minerals was determined:

Quartz	SiO ₂ 100 %	1,475
Chrysolite	" 40—45	1,610
Orthoclase	" 65	1,485

The last mineral, the pure K.Al.silicate consequently does not fit into the composed series. After mixing with some grains Fe₂O₃ (5—10 %) and fusing anew the index was raised to 1,510.

The method described above can be of practical use for a quick determination of the SiO₂ percentage of slags from the refractive index with an accuracy of $\pm 2\%$.

A word of thanks for the aid and advice to the Professors Dr. J. L. C. SCHROEDER VAN DER KOLK and S. J. VERMAES JR. may find a place here.

Mineralogy. — "*On an 'Eisenrose' of the St. Gotthard.*". By G. B. HOGENRAAD. (Communicated by Prof. J. L. C. SCHROEDER VAN DER KOLK).

Some time ago I tried to get a Hematite-streak with a so-called "Eisenrose." I did not succeed however, for to my astonishment the streak was not red but black. Several explanations came to my mind :

1°. that the mineral was somewhat friable, which was the cause that the streak could not consist of the very finest particles. But in rubbing the black colour remained; only the outlines showed a reddish-brown tint. The same was stated with about 25 other pieces of the same finding-place. So that the explanation proved to be not the right one.

2°. that the mineral contained Mn or Ti, since these elements have a great influence on the colour of the streak. But an analysis only produced little Ti and no trace of Mn, so that this explanation did not hold good either.

3°. that the mineral was magnetite. In its favour spoke the very distinct magnetism, stronger than hematite generally shows.

I then consulted some literature, to see whether anything had been written before on the streak, the magnetism and the chemical composition of "Eisenrose."

DANA says ¹⁾ :

St. Gotthard affords beautiful specimens, composed of crystallised tables grouped in the forms of rosettes (Eisenrosen), and accompanying crystals of adularia.

DANA calls this occurring Hematite, though he neither speaks of the chemical composition, nor gives any particulars about streak or magnetism.

In the "Zeitschrift für Krystallographie und Mineralogie von P. GROTH" I found in Number 13 on p. 301 a report by A. CATHREIN from STRÜVER's account on "Pseudomorphose von Magnetit nach Eisenglimmer von Ogliastra in Sardinien", written in the Atti della Reale Accademia Dei Lincei 1886. Volume II, 2°. Semestre, p. 331. The report in question follows here :

„Die Hauptmasse der Stufe besteht aus einem grobkörnigen Mineral, dessen unregelmässigen Individuen von mehreren Centimetern Durchmesser fest mit einander verwachsen erscheinen. Jedes Korn zerfällt nach einer Richtung äusserst leicht in dünnste Lamellen. Härte 6, Pulver schwarz, stark magnetisch, schwer schmelzbar, in Salzsäure leicht löslich. Diese Eigenschaften kommen dem Magnetit zu. Das Gemenge erscheint ganz frisch, unverändert und ursprünglicher Entstehung. Dass es sich hier nicht um nach {111} blätterig abgesonderten Magnetit handelt, folgt aus dem Mangel jeder Spur von Spaltbarkeit nach einer anderen Richtung ausser jener einen. Die Lamellarstruktur als Druckwirkung aufzufassen verbietet die Richtungsänderung der Lamellen in jedem einzelnen Korn. Nach des Verfassers Ansicht bleibt nur die Annahme einer Pseudomorphose von Magnetit nach Eisenglimmer.“

So this appearance as regards streak and magnetism corresponds with the specimen examined by me. Through the absence of a chemical analysis it cannot be decided in how far the supposition is right, that he had to do here with a pseudomorphosis from Magnetite to Eisenglimmer.

¹⁾ A System of Mineralogy p. 216.

In the "Zeitschrift der Geologischen Gesellschaft" Bd. 22, 1870 I found on page 719 in an article by G. VOM RATH the following statement ¹⁾:

"Pseudomorphische Massen von Magneteisen nach Eisenglanz. Farbe und Strich schwarz, schimmernd auf dem Bruch, magnetisch. Das Erz ist aber weder dicht, noch körnig (wie es sonst dem Magneteisen zukommt), sondern schuppig. Man erkennt sogar in einzelnen Drusen ganz deutlich die hexagonalen Formen des ursprünglichen Eisenglanzes; doch auch diese letzteren haben einen schwarzen Strich. Vermuthlich ist demnach jene ganze colossale Schichtenmasse bei Vallone ursprünglich Eisenglanz gewesen".

So to this can be applied what has been remarked on STRÜVER's article.

Finally D. F. WISER says ²⁾:

Die Eisen-Rosen vom Pomonetto wirken sehr stark auf die Magnet-Nadel. Das Strich-Pulver is dunkel-röthlichbraun, beinahe schwarz.

Die Wirkung auf die Magnet-Nadel is bei den Schweizerischen Eisenglanzen gar sehr verschieden, sowie die Nüanzirungen von Eisenschwarz bis Stahlgrau in ihrer Färbung. Bemerkenswerth scheint es mir, dass die Eisen-Rosen ohne aufliegende Rutil-Krystalle immer die schwärzeste Farbe zeigen, und dass dieselbe hingegend immer heller wird, je mehr Rutil auf den End-Flächen der Eisenglanz-Tafeln, ich möchte sagen, ausgeschieden worden ist.

Die Mineralien, welche die Eisen-Rosen vom Pomonetto begleiten, sind: kleine, graulich-weiße Adular-Krystalle, kleine sechseckige Tafeln von Tombackbraunen Glimmer und eine schmutzig grünlich-gelbe Rindenformige Substanz die vielleicht den Chloriten beigezählt werden darf.

Mein Freund, Hr Bergrath STOCKAR hieselbst, hat die Eisen-Rose vom Pomonetto analysirt und wird hoffentlich nächstens das Resultat seiner Untersuchungen veröffentlichen."

However I could not find this promised analysis anywhere in literature, so that I decided to do it myself (I). For a good control the same analysis was made by Messrs B. H. VAN DER LINDEN (II) and G. W. MALLÉE (III). The results of our investigations were as follows:

¹⁾ Geognostisch-mineralogische Fragmente aus Italiën, chapter VIII: Die Insel Elba, Zeitschr. D. G. G. 1870.

²⁾ Bericht über Mineraliën aus der Schweiz. N. Jahrb. 1854 p. 26.

	I.	II.	III.
Fe	69,94	69,13	69,50
O	29,97	29,60	30,46
accompanying mineral		1,2	
	<hr/> 99,91	<hr/> 99,93	<hr/> 99,96 ¹⁾

Reckoned for :

	Hematite	Magnetite
Fe	70	72,41
O	30	27,59.

So that my conclusion is that we have not to do with Magnetite but with Hematite.

The results of my researches are in consequence the following:

1st. That I have had to do with Hematite with very obvious magnetism and a black streak, which in rubbing along the outlines shows a brown tint (which generally every black streak does) and not with a pseudomorphosis from Magnetite to Hematite.

2nd. That where in literature of this occurrence of Hematite has been spoken, no analysis has been added, though the magnetism and the black streak have been observed more than once.

3rd. That it is desirable to convince oneself of the chemical composition with every "Eisenrose", which shows these characteristics.

Physics. — "*Contributions to the theory of electrons.*" I. By Prof. H. A. LORENTZ.

Simplification of the fundamental equations by the introduction of new units.

§ 1. If all quantities are expressed in electromagnetic units, as I have done in former papers, the relations between the volume-density ρ of the charge of an electron, the velocity v of its points, the

¹⁾ I here by have to mention that first the figure for the oxygen was determined by reduction in a hydrogen-current und weighing of the water absorbed by CaCl_2 ; that after that the figure for the iron was determined by dissolving the reduced mineral in dilute H_2SO_4 and making a titration of this solution (after reduction in a H_2S -current and after removing the H_2S by boiling in a CO_2 atmosphere) with a KMnO_4 -solution, of which 1 cM³ corresponded with 8,9 m.G. Fe.

The presence of Ti was shown as follows: the mineral was melted together with KHSO_4 , the fused mass dissolved in cold water. This solution together with H_2O_2 gave the well-known orange colour of TiO_3 . Moreover after adding a little HNO_3 , the Ti after having been boiled precipitated as white TiO_2 . The accompanying mineral, which in microscopic examination proved to be adularia, was removed as much as possible,

to be determined by means of (I)—(VI), a problem that may be reduced to equations of the form

$$\Delta\psi - \frac{1}{c^2} \frac{\partial^2 \psi}{\partial t^2} = -\alpha, \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

in which α is a known, and ψ an unknown function of x, y, z, t .

Let σ be any closed surface and n the normal to it, drawn outwards.

Then, if the equation (1) holds in the whole space S , enclosed by σ , we shall have for the value of ψ in a point P of this space, at the time t ,

$$\psi = \frac{1}{4\pi} \int_r^1 [\alpha] dS + \frac{1}{4\pi} \int \left\{ \frac{1}{r} \left[\frac{\partial \psi}{\partial n} \right] - [\psi] \frac{\partial}{\partial n} \left(\frac{1}{r} \right) \right\} d\sigma. \quad . \quad . \quad (2)$$

Here the first integral extends over the space S and the second over the boundary surface σ ; r is the distance to P , and the square brackets serve to indicate the values of the enclosed quantities for the time $t - \frac{r}{c}$.

Let us now conceive the surface σ to recede on all sides to infinite distance and let the circumstances be such that the surface-integral in (2) has the limit 0. Then, ultimately:

$$\psi = \frac{1}{4\pi} \int_r^1 [\alpha] dS, \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where the integration must be extended over infinite space.

§ 3. Equations of the form (1) may be deduced from the formulae (I)—(VI) in many different ways; they may e.g. be established for each of the components of \mathfrak{d} and \mathfrak{e} .¹⁾ The solution is however obtained in a simpler form²⁾, if one introduces four auxiliary quantities, a scalar potential φ and the three components $\mathfrak{a}_x, \mathfrak{a}_y, \mathfrak{a}_z$ of a vector-potential \mathfrak{a} . These quantities satisfy the equations

$$\Delta\varphi - \frac{1}{c^2} \frac{\partial^2 \varphi}{\partial t^2} = -\varrho,$$

$$\Delta \mathfrak{a}_x - \frac{1}{c^2} \frac{\partial^2 \mathfrak{a}_x}{\partial t^2} = -\frac{1}{c} \varrho \mathfrak{v}_x, \quad \Delta \mathfrak{a}_y - \frac{1}{c^2} \frac{\partial^2 \mathfrak{a}_y}{\partial t^2} = -\frac{1}{c} \varrho \mathfrak{v}_y, \quad \text{etc.},$$

so that, with the restrictions that are required if (3) is to be true, we may write

$$\varphi = \frac{1}{4\pi} \int_r^1 [\varrho] dS,$$

¹⁾ LORENTZ, La théorie électromagnétique de MAXWELL et son application aux corps mouvants, Arch. néerl. T. 25, p. 476 1892.

²⁾ See LEVI CIVITA, Nuovo Cimento, (4), vol. 6, p. 93, 1897; WIECHERT, Arch. néerl., (2), T. 5, p. 549, 1900.

$$a_x = \frac{1}{4\pi c} \int \frac{1}{r} [\varphi v_x] dS, \quad a_y = \frac{1}{4\pi c} \int \frac{1}{r} [\varphi v_y] dS, \text{ etc.}$$

After having found φ and \mathbf{a} , we may determine the dielectric displacement \mathbf{d} and the magnetic force \mathbf{h} by means of the relations ¹⁾

$$\mathbf{d} = -\frac{1}{c} \dot{\mathbf{a}} - \text{grad } \varphi, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

$$\mathbf{h} = \text{rot } \mathbf{a}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

It is to be remarked that the two potentials are not mutually independent; they are connected by the equation

$$\text{div } \mathbf{a} = -\frac{1}{c} \dot{\varphi}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

*Theorems corresponding to the principle of D'ALEMBERT
and that of least action.*

§ 4. The physicists who have endeavoured, by means of certain hypotheses on the mechanism of electromagnetic phenomena, to deduce the fundamental equations from the principles of dynamics, have encountered considerable difficulties, and it is best, perhaps, to leave this course, and to adopt the equations (I)—(VII) — or others, equivalent to them — as the simplest expression we may find for the laws of electromagnetism. Nevertheless, even if we prefer this point of view, it deserves notice that the fundamental equations may be transformed in such a way that we arrive at theorems of the same mathematical form as the general principles of dynamics. This has been done especially by ABRAHAM in his important paper "Principien der Dynamik des Elektrons" ²⁾. The considerations in this and the two next paragraphs agree with those of ABRAHAM, though presented in a form differing from his.

We shall consider a system of electrons moving in the infinitely extended aether, and we shall fix our attention on the different states of this system, the aether included, that succeed each other in the course of time in any electromagnetic phenomenon. From every one of these states we shall pass to another, differing infinitely little from it, and which we shall call the *varied* state. The variation or "virtual change" will consist in infinitely small displacements \mathbf{q} of

¹⁾ I shall write *grad* φ ("gradient of φ ") for the vector whose components are $\frac{\partial \varphi}{\partial x}, \frac{\partial \varphi}{\partial y}, \frac{\partial \varphi}{\partial z}$.

²⁾ DRUDE's *Annalen*, **10**, p. 105, 1903.

the points of the electrons, accompanied by infinitesimal changes in the dielectric displacement.

We shall write $\delta \mathbf{d}$ for the difference, in a fixed point of the æther, between the dielectric displacement before and after the virtual change, the sign of variation δ having a similar meaning when it precedes other symbols representing the value of some quantity in a definite point. If it is affixed to a letter representing a quantity belonging to the system as a whole, such as the total electric energy U , it will simply serve to indicate the difference between these values in the original or real and the varied states.

The variations to be considered are not wholly arbitrary. We shall limit our choice by supposing in the first place that each element of volume of an electron preserves its charge during the displacements \mathbf{q} ; this is expressed by the relation

$$\delta \varrho + \operatorname{div} (\varrho \mathbf{q}) = 0, \quad . \quad . \quad . \quad . \quad . \quad (7)$$

which may be compared to (II).

In the second place we shall suppose the variations of \mathbf{d} not to violate the condition (I).

In virtue of these restrictions the vector

$$\delta \mathbf{d} + \varrho \mathbf{q}$$

will present a solenoidal distribution. Indeed, we see from (I) that

$$\operatorname{div} \delta \mathbf{d} = \delta \varphi,$$

and here we may, according to (7), replace the right-hand member by $-\operatorname{div} (\varrho \mathbf{q})$.

Let us now conceive \mathbf{q} and $\delta \mathbf{d}$ to be chosen for every instant t , so that they vary continuously with the time. Then, in order completely to define the succession of varied states, or what we may call the "varied motion" of the system, we shall suppose the varied positions of the points of each electron to be reached at the same instants at which these points occupy the corresponding original positions in the real motion; we assume likewise that, in every point of space, the varied dielectric displacement exists at the same moments as the original one in the succession of real states.

By this the varied motion of electricity is entirely determined; indeed, since we know the velocity of matter and the rate at which \mathbf{d} changes, we are able to state what has become of the convection-current, the displacement-current, and also of the total current \mathbf{I} . The first thing we have to do will be to express $\delta \mathbf{I}$ in \mathbf{q} and $\delta \mathbf{d}$. Of course we may be sure beforehand that the distribution of both the new \mathbf{I} and the variation $\delta \mathbf{I}$ will be solenoidal. This must necessarily be the case, because we know 1st. that, in the states that succeed one another in the varied motion, each volume-element of

an electron retains its charge, and 2nd. that the condition (I) is continually fulfilled.

§ 5. Let us begin by considering $\delta \mathbf{v}_x$. This is the variation in a fixed point of space. Therefore, if $(\delta \mathbf{v}_x)$ is the variation for a definite point of an electron, we shall have

$$(\delta \mathbf{v}_x) = \delta \mathbf{v}_x + q_x \frac{\partial \mathbf{v}_x}{\partial x} + q_y \frac{\partial \mathbf{v}_x}{\partial y} + q_z \frac{\partial \mathbf{v}_x}{\partial z}.$$

As to $(\delta \mathbf{v}_x)$, it is easily shown to have the value

$$(\delta \mathbf{v}_x) = \frac{d\dot{q}_x}{dt},$$

if we understand by $\frac{d\dot{q}_x}{dt}$ the rate at which \dot{q}_x changes for a definite point of an electron. Comparing this to $\frac{\partial \dot{q}_x}{\partial t}$ or \dot{q}_x , the velocity of change in a fixed point of space, we get

$$(\delta \mathbf{v}_x) = \dot{q}_x + v_x \frac{\partial \dot{q}_x}{\partial x} + v_y \frac{\partial \dot{q}_x}{\partial y} + v_z \frac{\partial \dot{q}_x}{\partial z}.$$

These equations, combined with (7), lead us to

$$\begin{aligned} \delta I_x &= \delta (\dot{\mathbf{v}}_x + \varrho \mathbf{v}_x) = \delta \dot{\mathbf{v}}_x + \varrho \delta \mathbf{v}_x + v_x \delta \varrho = \\ &= \delta \dot{\mathbf{v}}_x + \varrho \dot{q}_x + \varrho v_x \frac{\partial \dot{q}_x}{\partial x} + \varrho v_y \frac{\partial \dot{q}_x}{\partial y} + \varrho v_z \frac{\partial \dot{q}_x}{\partial z} - \\ &- \varrho q_x \frac{\partial \mathbf{v}_x}{\partial x} - \varrho q_y \frac{\partial \mathbf{v}_x}{\partial y} - \varrho q_z \frac{\partial \mathbf{v}_x}{\partial z} - v_x \operatorname{div} (\varrho \mathbf{q}), \end{aligned}$$

or, if we add to the second member the first member of (II), multiplied by \dot{q}_x , after some further transformation,

$$\begin{aligned} \delta I_x &= \frac{\partial}{\partial t} (\delta \dot{\mathbf{v}}_x + \varrho \dot{q}_x) + \varrho v_x \frac{\partial \dot{q}_x}{\partial x} + \varrho v_y \frac{\partial \dot{q}_x}{\partial y} + \varrho v_z \frac{\partial \dot{q}_x}{\partial z} - v_x \operatorname{div} (\varrho \mathbf{q}) - \\ &- \varrho q_x \frac{\partial \mathbf{v}_x}{\partial x} - \varrho q_y \frac{\partial \mathbf{v}_x}{\partial y} - \varrho q_z \frac{\partial \mathbf{v}_x}{\partial z} + \dot{q}_x \operatorname{div} (\varrho \mathbf{v}) = \\ &= \frac{\partial}{\partial t} (\delta \dot{\mathbf{v}}_x + \varrho \dot{q}_x) + \frac{\partial}{\partial y} [\varrho (\dot{q}_x v_y - q_y \dot{\mathbf{v}}_x)] - \frac{\partial}{\partial z} [\varrho (\dot{q}_x v_z - q_z \dot{\mathbf{v}}_x)]. \end{aligned}$$

Here we may remark that the two last terms taken together represent the first component of the "rotation" of the vector whose components are

$$\varrho (q_y v_z - q_z v_y), \varrho (q_z v_x - q_x v_z), \varrho (q_x v_y - q_y v_x),$$

and that this vector is precisely the vector-product, multiplied by ϱ , of \mathbf{q} and \mathbf{v} . After having calculated δI_y and δI_z in the same way as δI_x , we may combine the results in the formula

$$\sigma l = \frac{\partial}{\partial t} (\sigma \mathfrak{d} + \varrho \mathfrak{q}) + \text{rot} \{ \varrho [\mathfrak{q} \cdot \mathfrak{v}] \} \quad . \quad . \quad . \quad . \quad . \quad (8)$$

What has already been said about the solenoidal distribution of σ is confirmed by this equation. The two vectors represented on the right hand side both have this property, the first by what we know of the vector $\sigma \mathfrak{d} + \varrho \mathfrak{q}$, and the second on account of the mathematical form in which it appears.

§ 6. We may next proceed to determine the variation σT of the magnetic energy. In doing so we shall start from the assumption that the varied motion of electricity involves a definite magnetic energy ¹⁾, to be determined as stated at the end of § 1.

The formula

$$T = \frac{1}{2} \int \mathfrak{h}^2 dS$$

leads immediately to

$$\sigma T = \int (\mathfrak{h}_x \sigma \mathfrak{h}_x + \mathfrak{h}_y \sigma \mathfrak{h}_y + \mathfrak{h}_z \sigma \mathfrak{h}_z) dS = \int (\mathfrak{h} \cdot \sigma \mathfrak{h}) dS,$$

where the integration covers all space. The same will be the case with the other volume-integrals appearing in the following transformations. If an integration is performed, or if the process of integration by parts is applied, one obtains integrals over the infinite surface which we may conceive as the boundary of the field of integration. These surface-integrals however will be supposed to vanish.

We begin by writing $\text{rot } \mathfrak{a}$ instead of \mathfrak{b} , as may be done in virtue of (5); and we shall next integrate by parts, keeping in mind that, on account of (V),

$$\text{rot } \sigma \mathfrak{h} = \frac{1}{c} \sigma l.$$

The result is

$$\sigma T = \int (\text{rot } \mathfrak{a} \cdot \sigma \mathfrak{h}) dS = \int (\mathfrak{a} \cdot \text{rot } \sigma \mathfrak{h}) dS = \frac{1}{c} \int (\mathfrak{a} \cdot \sigma l) dS, \quad . \quad (9)$$

or, if we substitute for σl its value (8),

$$\sigma T = \frac{1}{c} \int \left(\mathfrak{a} \cdot \frac{\partial}{\partial t} \{ \sigma \mathfrak{d} + \varrho \mathfrak{q} \} \right) dS + \frac{1}{c} \int \left(\mathfrak{a} \cdot \text{rot} \{ \varrho [\mathfrak{q} \cdot \mathfrak{v}] \} \right) dS. \quad (10)$$

Using (4), we may put for the first term

¹⁾ This assumption only means to define the value of T we shall assign to the wholly fictitious varied state.

$$\frac{1}{c} \frac{d}{dt} \int (\mathbf{a} \cdot \{\boldsymbol{\sigma} \mathbf{v} + \boldsymbol{\varrho} \mathbf{q}\}) dS - \frac{1}{c} \int (\dot{\mathbf{a}} \cdot \{\boldsymbol{\sigma} \mathbf{v} + \boldsymbol{\varrho} \mathbf{q}\}) dS = \\ = \frac{1}{c} \frac{d}{dt} \int (\mathbf{a} \cdot \{\boldsymbol{\sigma} \mathbf{v} + \boldsymbol{\varrho} \mathbf{q}\}) dS + \int (\mathbf{v} \cdot \{\boldsymbol{\sigma} \mathbf{v} + \boldsymbol{\varrho} \mathbf{q}\}) dS + \int (\text{grad } \varphi \cdot \{\boldsymbol{\sigma} \mathbf{v} + \boldsymbol{\varrho} \mathbf{q}\}) dS. \quad (11)$$

Now, it appears from (9) that

$$-\frac{1}{c} \int (\mathbf{a} \cdot \{\boldsymbol{\sigma} \mathbf{v} + \boldsymbol{\varrho} \mathbf{q}\}) dS \dots \dots \dots (12)$$

is the change the magnetic energy of the system would undergo, if we gave to the current the change $\boldsymbol{\sigma} \mathbf{v} + \boldsymbol{\varrho} \mathbf{q}$. We shall write $\boldsymbol{\sigma}' \mathbf{l}$ for *this* variation of the current, and $\boldsymbol{\sigma}' \mathbf{h}$, $\boldsymbol{\sigma}' T$ for the corresponding variations of \mathbf{h} and T . As to $\boldsymbol{\sigma}' \mathbf{l}$, it may be defined as the current that would exist if the changes represented by \mathbf{q} and $\boldsymbol{\sigma} \mathbf{v}$ were accomplished in unit of time.

On the other hand, $\int (\mathbf{v} \cdot \boldsymbol{\sigma} \mathbf{v}) dS$ is the variation of the electric energy U and the last integral in (11) is 0, because the vector $\boldsymbol{\sigma} \mathbf{v} + \boldsymbol{\varrho} \mathbf{q}$ is solenoidally distributed. Thus, the first term in (10) becomes

$$\frac{d\boldsymbol{\sigma}' T}{dt} + \boldsymbol{\sigma} U + \int (\mathbf{v} \cdot \boldsymbol{\varrho} \mathbf{q}) dS.$$

For the last term in that equation we find, integrating by parts,

$$\frac{1}{c} \int (\text{rot } \mathbf{a} \cdot \{\boldsymbol{\varrho} [\mathbf{q} \cdot \mathbf{v}]\}) dS = \frac{1}{c} \int \boldsymbol{\varrho} (\mathbf{h} \cdot [\mathbf{q} \cdot \mathbf{v}]) dS = \frac{1}{c} \int \boldsymbol{\varrho} (\mathbf{q} \cdot [\mathbf{v} \cdot \mathbf{h}]) dS,$$

so that finally

$$\boldsymbol{\sigma} T = \frac{d\boldsymbol{\sigma}' T}{dt} + \boldsymbol{\sigma} U + \int \boldsymbol{\varrho} \left(\mathbf{q} \cdot \left\{ \mathbf{v} + \frac{1}{c} [\mathbf{v} \cdot \mathbf{h}] \right\} \right) dS.$$

Now, the equation (VII) shows that the last term is precisely the work done, during the displacements \mathbf{q} , by the electric forces exerted by the aether on the electrons.

Writing $\boldsymbol{\sigma} E$ for this work, we have

$$\boldsymbol{\sigma} E = \boldsymbol{\sigma} (T - U) - \frac{d\boldsymbol{\sigma}' T}{dt} \dots \dots \dots (13)$$

an equation closely corresponding to D'ALEMBERT's principle in common dynamics.

§ 7. The motion of the electrons themselves may be determined by ordinary methods; it will be governed by the electric forces whose work has been denoted by $\boldsymbol{\sigma} E$, together with forces of any other kind that may come into play. We shall confine ourselves to those cases in which these latter forces depend on a potential energy U_1 ; then the total virtual work of all forces acting on the

electrons will be $\delta E - \delta U_1$. Moreover we shall ascribe to the electrons a certain kinetic energy T_1 , which they have by virtue of their mass in the ordinary sense of the word. Should there be no such "true" mass, we have only to put $T_1 = 0$.

One of the forms that may be given to the variational equation of motion for a system of material particles is

$$\delta A = \frac{d\delta' T_1}{dt} - \delta T_1,$$

δT_1 being the change of T_1 , if we pass from the real motion to some varied motion in which the varied positions are reached at the same moments as the original positions in the real motion, δA the virtual work of the forces, and $\delta' T_1$ the increment that would be acquired by the kinetic energy T_1 , if variations, equal to the virtual changes of the coordinates, were imparted to the corresponding velocities (the coordinates themselves being kept constant). For our system of electrons

$$\delta A = \delta E - \delta U_1;$$

hence, if we use for δE the formula (13),

$$\delta \{ (T + T_1) - (U + U_1) \} - \frac{d\delta' (T + T_1)}{dt} = 0.$$

We shall finally multiply this by dt and integrate from t_1 to t_2 . In case both the displacements \mathfrak{q} and the variations $\delta \mathfrak{b}$ vanish at the limits, we find

$$\delta \int_{t_1}^{t_2} \{ (T + T_1) - (U + U_1) \} dt = 0.$$

This is analogous to the principle of least action.

§ 8. In what precedes there has been question of the variations of the energies T and U , taken for the system of electrons together with the surrounding aether, which extends to infinite distance. Similar though somewhat less simple results are obtained, if one understands by T and U the magnetic and the electric energies, in so far only as they belong to the space within an immovable closed surface σ . In what follows it is to be understood that this surface may have, relatively to the system of electrons, any position we like; for simplicity's sake however we shall suppose that it cuts none of them, so that, in every point of σ , the density $\rho = 0$. As to the virtual variations, determined by \mathfrak{q} and $\delta \mathfrak{b}$, they need not at all be confined to the part of the system within the surface. We shall denote by n the normal to the surface, drawn towards the

outside, and by λ, μ, ν the angles between this normal and the positive axes of coordinates.

If now we repeat the above calculations, we have to do with volume-integrals confined to the space within σ , and every integration by parts will give rise to a surface-integral.

Thus, to the last member of (9) we shall have to add the term

$$\int \begin{vmatrix} \cos \lambda, & \cos \mu, & \cos \nu \\ a_x, & a_y, & a_z \\ \delta h_x, & \delta h_y, & \delta h_z \end{vmatrix} d\sigma = \int [a \cdot \delta h]_n d\sigma$$

and the value of (12) will no longer be $\sigma' T$, but

$$\sigma' T - \int \begin{vmatrix} \cos \lambda, & \cos \mu, & \cos \nu \\ a_x, & a_y, & a_z \\ \sigma' h_x, & \sigma' h_y, & \sigma' h_z \end{vmatrix} d\sigma = \sigma' T - \int [a \cdot \sigma' h]_n d\sigma. \quad (14)$$

The last integral of (11) becomes

$$c \int (\text{grad } \varphi \cdot \{\text{rot } \sigma' h\}) dS = c \int (\text{rot grad } \varphi \cdot \sigma' h) dS - c \int [\text{grad } \varphi \cdot \sigma' h]_n d\sigma \quad (15)$$

Here the first term on the right-hand side is 0, since $\text{rot grad } \varphi = 0$. The transformation of the last part of (10) remaining as it was, as we have supposed $\varrho = 0$ in all points of the surface, we finally find for the second member of (13) the additional term

$$\int \left\{ -[a \cdot \delta h]_n + \frac{\partial}{\partial t} [a \cdot \sigma' h]_n + c [\text{grad } \varphi \cdot \sigma' h]_n \right\} d\sigma.$$

But, on account of (4),

$$\begin{aligned} & \frac{\partial}{\partial t} [a \cdot \sigma' h]_n + c [\text{grad } \varphi \cdot \sigma' h]_n = \\ & = \left[a \cdot \left\{ \frac{\partial \sigma' h}{\partial t} \right\} \right]_n + [a \cdot \sigma' h]_n + c [\text{grad } \varphi \cdot \sigma' h]_n = \\ & = \left[a \cdot \left\{ \frac{\partial \sigma' h}{\partial t} \right\} \right]_n - c [v \cdot \sigma' h]_n, \end{aligned}$$

We get therefore, instead of (13),

$$\delta E = \sigma(T - U) - \frac{d\sigma' T}{dt} + \int \left\{ \left[a \cdot \left\{ \frac{\partial \sigma' h}{\partial t} - \sigma h \right\} \right]_n - c [v \cdot \sigma' h]_n \right\} d\sigma \quad (16)$$

§ 9. The following are some examples of the applications that may be made of the formulae (13) and (16).

a. Let the virtual changes in the position of the electrons and in the dielectric displacement be proportional to the rates of change in the real motion, i. e. let

$$\delta q = \varepsilon v, \quad \delta d = \varepsilon \dot{d},$$

ε being a constant infinitely small factor. From these assumptions it follows at once that

$$\sigma' l = \varepsilon l, \quad \sigma' h = \varepsilon h.$$

Now the magnetic energy may be considered as a homogeneous quadratic function of the components of the current; it will therefore change in ratio of 1 to $1 + 2\varepsilon$, if the current becomes $(1 + \varepsilon)l$. Thus: $\sigma' T = 2\varepsilon T$.

We may also infer from our assumptions that the position of the electrons and the values of \mathfrak{d} are, in the varied motion at the time t , what they are in the real motion at the time $t + \varepsilon$, so that the only difference between the two motions is that the one is in advance of the other by an interval ε .

In this way it is seen that

$$dT = \varepsilon \frac{dT}{dt}, \quad dU = \varepsilon \frac{dU}{dt}, \quad d\mathfrak{h} = \varepsilon \frac{\partial \mathfrak{h}}{\partial t}, \quad \frac{\partial \sigma' \mathfrak{h}}{\partial t} - \sigma' \dot{\mathfrak{h}} = 0.$$

Substituting these values in the equation (16), we get, after division by ε and multiplication by dt , denoting by dE the work done by the electric forces in the real motion, during the time dt ,

$$dE = -d(T + U) - c dt \int [\mathfrak{d} \cdot \mathfrak{b}]_n d\sigma. \quad . \quad . \quad . \quad (17)$$

This is the equation of energy. The last term represents the flow of energy through the surface.

b. Applying (17) to a single electron, whose motion is a translation with variable velocity along a straight line, one may calculate the force with which it is acted on by the aether, and which, under certain simplifying assumptions, is found to be proportional to the acceleration and directed oppositely to it. The quotient of this force, divided by the acceleration, may appropriately be called the *electromagnetic mass* of the electron.

c. There will likewise be a force proportional and opposed to the acceleration, if the latter is perpendicular to the direction of motion. In this case however, of which the uniform motion of an electron in a circle furnishes the simplest example, we must recur to the equation (16), in order to determine the force. The surface σ may be supposed to lie at infinite distance and the virtual displacement must be taken in the direction of the acceleration. The ratio of the force and the acceleration may again be called the *electromagnetic mass*, though, except for small velocities, its value is not equal to that of the corresponding ratio in the case *b*.

In both cases the result agrees with what has been found by ABRAHAM.

Ponderomotive action on a system of electrons.

§ 10. A virtual change of a very simple kind is an infinitely small translation of all the electrons, combined with what we may call an equal translation in the same direction of the whole electric field. Applying to these variations — which we give as well to the part of the system outside the surface σ as to the part enclosed by it — the equation (16), one may calculate the resulting force exerted by the aether on the electrons within the surface. This force may be shown to consist of two parts, the first of which is the force with which we should have to do, if the surface σ were subjected to the stresses in the aether, whose components have been already determined by MAXWELL, whereas the second part is determined by the rate of change of a certain integral, relating to the space S within σ . The latter part will therefore vanish if the state is stationary, and may be left out of account if, for periodic states, we wish only to know the mean value of the resulting force, taken for a full period. I need not here work out the formulae, having formerly deduced the result in a more direct way. The components of MAXWELL's stress are

$$\left. \begin{aligned} X_x &= \frac{1}{2} (\mathfrak{d}_x^2 - \mathfrak{d}_y^2 - \mathfrak{d}_z^2) + \frac{1}{2} (\mathfrak{h}_x^2 - \mathfrak{h}_y^2 - \mathfrak{h}_z^2), \text{ etc.} \\ X_y &= Y_x = \mathfrak{d}_x \mathfrak{d}_y + \mathfrak{h}_x \mathfrak{h}_y, \text{ etc.} \end{aligned} \right\} \quad (18)$$

and the just mentioned volume-integral is

$$-\frac{1}{c^2} \int \mathfrak{E}_h dS,$$

\mathfrak{E}_h being the flux of energy in the direction h , for which we seek the resulting force.

Thus, the resulting force in the direction of x is given by

$$\mathfrak{E} = \int X_n d\sigma - \frac{1}{c^2} \frac{d}{dt} \int \mathfrak{E}_x dS. \quad . \quad . \quad . \quad . \quad . \quad (19)$$

The vector $\frac{1}{c^2} \int \mathfrak{E} dS$ is called by ABRAHAM the *electromagnetic momentum*.

§ 11. Similar results would be obtained if we chose for the virtual variation, instead of a translation, an infinitely small rotation about an axis passing through the origin of coordinates; the equation (16) would then serve to determine the resulting couple, arising from all the forces exerted by the aether on the electrons within the surface σ . The moment of this couple may however be calculated

in a shorter way, if we start from what we know already about the forces.

Indeed, in virtue of the formula (19) and the two corresponding to it, the components of the force acting on an element of volume dS may be represented as follows :

$$\left. \begin{aligned} X dS &= \left(\frac{\partial X_x}{\partial v} + \frac{\partial X_y}{\partial y} + \frac{\partial X_z}{\partial z} \right) dS - \frac{1}{c^2} \dot{\mathfrak{E}}_x dS, \\ Y dS &= \left(\frac{\partial Y_x}{\partial x} + \frac{\partial Y_y}{\partial y} + \frac{\partial Y_z}{\partial z} \right) dS - \frac{1}{c^2} \dot{\mathfrak{E}}_y dS, \\ Z dS &= \left(\frac{\partial Z_x}{\partial x} + \frac{\partial Z_y}{\partial y} + \frac{\partial Z_z}{\partial z} \right) dS - \frac{1}{c^2} \dot{\mathfrak{E}}_z dS \end{aligned} \right\} \dots \quad (20)$$

and these formulae give immediately for the components of the couple

$$\int (yZ - zY) dS = \int (yZ_n - zY_n) d\sigma - \frac{1}{c^2} \int (y\dot{\mathfrak{E}}_z - z\dot{\mathfrak{E}}_y) dS. \quad (21)$$

§ 12. Another consequence of the equations (20), analogous to the well known virial-theorem in ordinary kinetic theory, will perhaps be thought of some interest. In order to find it, we have only to add the three equations, multiplied by x, y, z , and to integrate the result over the space S , within the surface σ . Transforming such terms as $\int x \frac{\partial X_x}{\partial x} dS$ by means of partial integration, we find

$$\begin{aligned} \int (Xx + Yy + Zz) dS &= \int (X_n x + Y_n y + Z_n z) d\sigma - \\ &- \int (X_x + Y_y + Z_z) dS - \frac{1}{c^2} \frac{d}{dt} \int (\mathfrak{E}_x x + \mathfrak{E}_y y + \mathfrak{E}_z z) dS. \quad (22) \end{aligned}$$

For stationary states the last term will vanish, so that, if we substitute in the term preceding it the values (18),

$$\int (Xx + Yy + Zz) dS = \int (X_n x + Y_n y + Z_n z) d\sigma + T + U.$$

Particular cases of ponderomotive action.

§ 13. In a large variety of cases, in which the system of electrons is confined to a space of finite dimensions, the electric and magnetic intensities in the surrounding field become so feeble at great distances that the surface-integrals in (19) and (21) approach the limit 0, if the surface σ moves to infinite distance. Moreover, the volume-integrals will vanish if the state is stationary. We then come to

the conclusion that the resulting force and the resulting couple are 0 for the whole system. If the system consists of two parts A and B , we may express the same thing by saying that the total ponderomotive action on one of these is equal and opposite to the total action on the other.

Of course this will be equally true if, for a system whose state changes periodically, we have only in view the mean ponderomotive action during a full period.

These theorems are useful whenever the phenomena in one of the parts, say in A , are not well enough known to permit a direct calculation of the force acting on this part of the system. If the phenomena in B are less complicated, so that we encounter no difficulty in determining the force or the couple acting on this part, the action on A will be found at the same time.

We may apply this in the first place to well-known experiments on electromagnetic rotations.

Let us consider a cylindrical magnet, touched in two points of its surface by the ends of a conducting wire W . Let this wire be the seat of an electromotive force, producing a current that flows through W and through part of the magnet. The ponderomotive forces acting on the wire are known with certainty and may easily be deduced from the formula (VII); they produce a couple, tending to turn the wire about the axis of the magnet. Without entering into any speculations concerning the motion of the electrons in its interior, we may infer that the magnet will be acted on by an equal couple in the opposite direction.

Of course this reasoning must be justified by showing that the surface-integral in (21) is really 0, if it is taken for a surface at infinite distance. This is readily seen to be the case, if we keep in mind that, at great distances, the magnetic force produced by the system varies inversely as the third power of the distance, and that the intensity of the electric field, if it exist at all, will certainly contain no terms diminishing more slowly than the square of the distance.

§ 14. I shall choose as a second example some experiments, lately made by WHITEHEAD¹⁾ for the purpose of testing a consequence of MAXWELL's theory that has been admitted by many physicists and is unavoidable in the theory of electrons, viz. that a ponderable dielectric, which is the seat of a variable dielectric displacement, and therefore of a displacement-current, when placed in a magnetic

¹⁾ WHITEHEAD, Ueber die magnetische Wirkung elektrischer Verschiebung, *Physikalische Zeitschr.*, 4, p. 229, 1903.

field, will be acted on by a similar force as a body carrying a conduction-current. In WHITEHEAD's apparatus two cylindric metallic plates, having the same vertical axis PQ , formed a condenser, in which a rapidly alternating electric field was maintained; at the same time alternating currents were passed through the horizontal windings of a circular coil, surrounding the condenser; the axis of the coil, which is at the same time the axis of its magnetic field, coincided with PQ . A sensitive torsion-balance was suspended by a wire passing along the axis of the instrument; the ends of the beam carried each a piece of some solid dielectric, so that these two equal pieces hung, diametrically opposite each other, in the air-space between the condenser-plates. The two fields, the electric and the magnetic, had exactly the same period, being produced by the same alternate current-machine; besides, the arrangements were such that there was a phase-difference of a quarter period between the two fields. Thus, at the instants at which the magnetic force had its maximum values, the rate of change of the electric field and consequently the intensity of the displacement-current was likewise at its maximum. Under these circumstances a sensible couple acting on the dielectric was expected, but no deviation of the beam, attributable to such a couple, could with certainty be observed.

We may remark in the first place that in WHITEHEAD's formula for the expected effect, the specific inductive capacity K appears in the numerator. If this were right, a couple would act on the aether between the plates itself. According to the theory of electrons, as here presented, ponderomotive force acts only on the electrons contained in ponderable bodies, but in no case on the aether. The theory therefore regards every ponderomotive action as due to the *difference* between the properties of the body acted upon and the aether; it can lead to a formula containing in the numerator $K-1$, but never to one, containing, instead of this factor, the coefficient K itself.

In the second place WHITEHEAD has overlooked a circumstance by which the effect he sought for must have been, at least for the greater part, compensated. The compensation may be shown to be complete if the properties of the dielectric used differ from those of the aether to so small extent, that quantities which are in this respect of the second order of magnitude, i. e. of the order $(K-1)^2$, may be neglected.

If this may be done, the ponderomotive action on a ponderable dielectric, placed between the condenser-plates, may be considered not to be altered by the presence in the field of a second or third piece of the same dielectric. Now, the two bodies suspended at the ends of WHITEHEAD's torsion-balance may be taken to have been parts of a

complete dielectric ring, bounded by a surface of revolution with the axis PQ . Moreover it will be safe to assume that the action on the two bodies which it was sought to observe, did not depend on their relative positions with respect to the wires leading to the condenser-plates, and remained therefore the same, in whatever position the torsion-balance was turned. If this was the case, the action on a body that is the n^{th} part of the ring (being cut out of it by two planes passing through the axis) must have been the n^{th} part of the couple, acting on the complete ring. Consequently, it will suffice to show that the effect is 0, if the experiment is made with a complete dielectric ring.

§ 15. For simplicity's sake we shall suppose the condenser-plates to be united by a wire W and their alternating electric charges to be produced by a periodic electromotive force in this wire. As to the currents in the coil, they may be regarded as due to electromotive forces of the same period, acting in the windings themselves; indeed, the action on the dielectrics can only depend on the magnetic field and not on the way in which it is produced. For this same reason it is allowable to ascribe to the windings so small a resistance that they do not carry any appreciable charges.

Then no other but electromagnetic forces will act on the windings of the coil and these cannot give rise to any couple about the axis PQ , because such forces are perpendicular to the elements of the windings. By the theorem of § 13 the couple acting on the torsion-balance must therefore have been equal and opposite to the moment of rotation, acting on the condenser-plates and the wire W . It remains to show that this last moment has been 0.

I shall denote by I the electromotive forces acting in the connecting wire W , by II those existing in the windings of the coil, and I shall distinguish by the suffixes 1 and 2 the states arising from these two causes. Let us indicate by A_1 the charges of the plates and the currents in these and the wire W , in so far as they are due to I, and let A_2 have the same meaning with respect to II; also, let F_1 and F_2 be the electromagnetic fields excited by the two causes. In each of these fields there will be an electric force \mathfrak{d} (acting on charges that are in rest), as well as a magnetic force \mathfrak{h} ; in virtue of the first, the field will exert a ponderomotive force on the charges of the plates and in virtue of the second on the currents, one of these actions being determined by the first, and the other by the last term in the general equation (VII). If we denote by the symbol (F, A) the couple acting on the plates and the wire, in so far as it is due

to a field F and a state A of these bodies, the two actions we shall have to consider may be represented by

$$(F_1, A_2) \text{ and } (F_2, A_1).$$

The first of these is readily seen to be 0. Indeed, the magnetic field, produced by the forces II, though modified by the presence of the dielectric ring, is symmetrical around the axis PQ . Therefore, if the periphery of the condenser-plates is nowhere interrupted, the state A_2 will consist in circular currents in these plates, without any electric charge. It is impossible that the field F_1 should, by its action on these currents, give rise to a couple, since, whatever be the nature of this field, each element of the stream-tubes will only be acted on by a force perpendicular to its length.

In reality the case was somewhat different, each condenser-plate being cut by a vertical slit. There must have been equal and opposite charges at the edges of each slit and the field F_1 must have acted on these charges, in virtue of the electric force existing in it. These forces may however be supposed to have annulled each other, because the distance between the charges on the two edges was very small.

§ 16. The action (F_2, A_1) is therefore the only one that remains to be considered. Now, in the state A_1 , the plates of the condenser were the seat of charges, whose amount was modified by the influence of the dielectric ring, and whose alternations were accompanied by currents in the wire W and in part of the plates themselves. In so far as they are currents of conduction, i. e. in so far as they consist in a motion of electrons, these currents are evidently unclosed. We may decompose the whole system of them into infinitely thin stream-tubes, the tubes being all thronged together in the connecting wire, and widening out in the plates, at whose surfaces each stream-tube ends in two elements of surface.

Let S be one of the stream-tubes, G the end of it on the outer, and H that on the inner plate, e the charge in G , $-e$ that in H ,

$$i = \frac{de}{dt} (23)$$

the current in the tube in the direction from H towards G , and let us consider the action (F_2, A_1) only in so far as it depends on this current i and on the charges e and $-e$.

In the first place there will be an electromagnetic force on the tube S , owing to the current i . The couple arising from it depends on the course of the magnetic lines of force in the field F_2 ; it is most easily found by remarking that its work during a complete

and the couple to be added to (24) will be given by

$$-\frac{1}{2\pi c} e \frac{dN}{dt}.$$

Taking into account (23), we find for the total couple

$$-\frac{1}{2\pi c} \left(i N + e \frac{dN}{dt} \right) = -\frac{1}{2\pi c} \frac{d(eN)}{dt}.$$

Since this is the rate of change of a periodic quantity, the mean value will be 0, as above asserted.

The above somewhat complicated reasoning has been used in order to avoid the difficulties arising in a closer examination of the phenomena going on in the ponderable dielectrics. The result may however be verified by making suitable assumptions concerning these phenomena. It will suffice for our purpose to replace one of the dielectric bodies by a single pair of electrons A and B , the first of which is immovable, whereas the second may be displaced over an infinitely small distance, in a radial direction, by the electric forces of the field F_1 . We shall denote by $-e$ and $+e$ the charges of A and B , by r the distance of A to the axis, by s the infinitely small distance AB , and we shall write \mathfrak{h}_z for the vertical component of the magnetic force in the field F_2 and D for the value of the electric displacement in this field at a distance r from the axis. We shall take the positive directions as follows: for s outwards, for \mathfrak{h}_z upwards, and for D along the circular line of electric force in a direction corresponding to the positive direction of \mathfrak{h}_z , i. e. in the direction of a positive rotation about the axis.

Now, owing to the velocity $\frac{ds}{dt}$ of the electron B , there will be, according to the formula (VII), a force

$$-\frac{e}{c} \mathfrak{h}_z \frac{ds}{dt}$$

acting on this electron along a circle about the axis, and producing a moment

$$-\frac{e}{c} r \mathfrak{h}_z \frac{ds}{dt} (24')$$

This is the couple of which WHITEHEAD has sought to prove the existence. It is however annulled by the moment arising from the action of the field F_2 in virtue of its electric force D . For the particle A this moment is

$$-e r D$$

and for the particle B it is obtained if we replace $-e$ by $+e$,

stant temperature, laid down in the previous communication have all been applied in this arrangement, a vigorous stirring with the ring shaped valved-stirrer, the adjustment at the desired temperature to the indication of a sensitive indicator by regulating the pressure at which the liquid boils while reading a differential oil-manometer made for the purpose, and lastly the determination of the temperature of observation as corresponding with the mean obtained graphically of the readings of the thermometer (as in § 5).

Plate V shows in detail the differences in the construction between this form and the former plates I and II (and also Plate I Comm. 51), the parts unaltered remaining are indicated by the same letters as before, and the modified parts by letters with accents, while entirely different parts have new letters.

The height of the vacuumglass B'_0 , is so chosen that the liquefied gas cannot be blown out; and the glass itself has been silvered, leaving open two opposing windows V'_2 . Through these the phenomena in the experimental tube may be watched, and from the position of an aluminium wire fastened to a cork float the depth of liquefied gas may be derived. If the insulating power of the vacuumglass is not perfect, condensation of moisture on its outer wall may be avoided by placing it into a beaker filled with alcohol, which if necessary is renewed when cooled. Thus the same principle is followed which was employed when necessary in the case of the cryostat (Comm. 51) when the windows had to be kept clear and where hot dry air was drawn through the outer spaces of the observing glasses (V_2 , see Pl. I of this Comm. and for the details pl. I Comm. 51).

The vacuum glass and the auxiliary apparatus are supported by a copper cover N'_{00} , with its rim tinned to protect it from the action of the india-rubber ring N'_1 , and which, like the cryostat of § 1, has been coated with polished nickel-paper. To this cover are fastened the exit tube of the gas T'_1 , and the safety tube Y'_{02} , the connection X'_2 with the oil manometer (for details see plate I) and a copper tube N'_{01} , into which the india rubber stopper is placed holding the apparatus to be immersed in the bath (in our case the piezometer for the critical phenomena K_r , and the correction thermometer ξ_{01} with its leads ξ_{00} (comp. § 1) while the thermo-element Θ may be considered as forming an inherent part of the cryostat). There is also a tube through which the capillary a_1 admitting the liquefied gas is led and where it is supported by a piece of cork a'_{13} . It is closed by means of an india-rubber tube a'_{12} drawn over the tube and a thin cap soldered on to a_1 .

Between the cover and the rim of the vacuum glass a wooden

cylindrical jacket N'_3 is placed resting against the latter by means of an india-rubber ring N'_2 . Two cylinders N'_4, N'_6 of nickel-paper serve to diminish radiation, especially in the direction of the delivery tube.

As mentioned the frame which keeps the protecting cylinder in its place is fastened to the cover. For a complete explanation of the letters and parts of both this and the stirrer reference may be made to § 4. Further we may note that ξ_1 is fastened with silk cords to ξ'_2 and this again with silk cords to the cover N'_{00} , while ξ'_2 is supported by the glass tube ξ_4 fitting onto the pins ξ'_5 .

The three threads χ_1 on which the stirrer hangs are led directly through the three india-rubber tubes χ'_{61} , connected hermetically to tubes soldered onto the cover and fitting hermetically onto the threads at χ'_{62} , to the brass disc χ'_{63} and rod χ'_{64} which is connected by a small chain χ'_{65} passing over a pulley χ'_{66} to the motor by means of a steelwire. The arm of the motor may be adjusted to different throws, while velocity of rotation can be regulated by means of a rheostat.

The mounting of the apparatus is very simple. The stopper with the measuring apparatus is placed into the tube N'_{01} of the cover, to which all the auxiliary apparatus has been connected, then the vacuum glass is slid into the india-rubber ring which is also connected to the cover and is fastened there by means of tightening bands. In order to secure an airtight fit the india-rubber on the metal and on the glass has been coated beforehand with a solution of indiarubber in benzine.

With a view to the description given in III the operations for the adjustments at given temperature require amplification only in a few points. In the case considered here, the evaporated gas was led back through the exit tube to the gasholder or to the large exhausted reservoir of the ethylene circulation in the cryogenic laboratory (Comm. 14, Dec. '94) whence the ethylene was further condensed into the condenser immersed in methyl chloride. As described in Comm. 14 the circulations of the cryogenic laboratory have been so arranged that they may be used at any time. Besides the reservoirs that have to be exhausted, a permanent part of the circulation consists in branched tubes with cocks as shown on plates I and IV. The cryostat had only to be connected to the circulation in order to be easily brought to the required pressure. In the case considered here the experiments were not made in the cryogenic laboratory but in an other room and the length of the lead a'_{31} was 10 m. Although the liquid ethylene had to be conducted over such a distance, yet

the adjustment of the bath to the required temperature (say at -120°) was obtained within one hour after the pumps in the cryogenic laboratory had been set working.

Instead of a resistance thermometer, to regulate the temperature, we used the thermoelement Θ , the protected junction being placed at the side of the piezometer (comp. comm. 27 June '96); it is visible through the window V' , (in plate IV). The electro-motive power of the thermoelement is compared by means of the zero method with that of a thermoelectric control element or a WESTON-element.

For the same difference of temperature the deflections on the scale of the sensitive galvanometer were almost as large as in the measurements made with the resistance thermometer (comp. § 5). An example of the determination of the temperature is not necessary in addition to Plate III.

IV. *A permanent bath of liquid nitrogen at ordinary or reduced pressure.* In Comm. 14 (Dec. '94) a short description was given of the temperature steps obtained by means of circulations of methylchloride, ethylene and oxygen. In connection with that description I mentioned my intention of adding more circulations to those already existing and said that I hoped to replace more and more parts of the existing circulations by greater and to insert such technical apparatus as should be found advisable so that the existing apparatus could be used in the new circulations with pure or costly gases. An example of this is the circulation of nitrogen added to the existing temperature cascade, of which a description is now required by the completion of some of the measurements rendered possible by it. For measurements at temperature between -195° C. and -210° C. a nitrogen is much to be preferred to an oxygen-circulation as the tension at which the oxygen boils at -195° is so small that accurate regulation at constant temperature becomes very difficult. As the preparation of pure nitrogen in such large quantities as a circulation requires presents many difficulties, the compressor and the vacuum pump must be suitable and efficient. These conditions are fulfilled by the mercury and the auxiliary compressors which are generally used for the compression of pure gas and which in the originally temperature cascade served for the oxygen circulation. However when the BROTHERHOOD compressor (comp. Comm. 14 Dec. '94 and 51 Sept. '99) could be used for the oxygen circulation in the cascade they could be used for the nitrogen circulation.

The nitrogen is prepared from sodium nitrite. Besides being passed through ferrous sulphate and sulphuric acid it is led over hot cop-

per and then again through ferrous sulphate and sodium hydroxide, because otherwise traces of nitric oxide might be left and this blocks the cocks (this gas is recognised at once by a strong smell of higher oxides of nitrogen when it mixes with the air). In order to remove traces of this oxide, I have sometimes added to the gas a quantity of oxygen as nearly as possible equivalent to the NO contained therein and have then passed it through sodium hydroxide. The gas is collected and provisionally kept in galvanised iron vessels holding 1 M³. From these it is driven out later by water heated by a steam jet and after passing through sodium hydroxide and sulphuric acid it is forced into a small gasholder floating on oil and holding 500 L. By means of the auxiliary compressor *AC* lubricated with glycerine (see Pl. VI and for details Comm. 54 Sept. '99) and the mercury compressor *HgC* (see Pl. VI and for details Comm. 54) the gas is forced over into a metal cylinder of 18 liters capacity after passing through the drying tubes *D*₁, *D*₂ filled with caustic soda in the form of sticks.

Plate VI shows the scheme of the entire circulation with the cryostat *Cr*, into which the liquid nitrogen is admitted at *a* and where it evaporates under ordinary or reduced pressure at the desired temperature. The whole arrangement has been used in the comparison of the platinum resistance thermometer with the hydrogen thermometer, which has been mentioned in III. The apparatus themselves are drawn diagrammatically but in their true proportions, while the connections are entirely schematic. A detailed representation of the cryostat with the auxiliary apparatus appertaining to it for uniform and constant temperatures will be found on plate I where the same letters have been used. On the other hand plate VI may be considered as a supplement to plate I. Nothing is wanting for a complete representation of the circulation except the gasholder and the vacuum vessel of 5 M³. (comp. § 5 for its use) which are too large to be represented on the same drawing as the parts given. There is an insignificant difference in the coupling of the leads between plate I and plate VI, for on plate VI *Exh.* 1' indicates the connection of the compression side of a BURCKHARDT—WEISS vacuum pump *Bu Vac.*, described below into which the exhaust *Exh.* 2 terminates, to an exhaust pump (which may also be *AC* of the circulation). Moreover next to the lead from *Y*₁ to *Y*₃₆ we have drawn what must be substituted for it in comparison with the arrangement on plate IV.

RN is the cylinder where the nitrogen has been compressed by means of *AC* and *HgC* through the drying tubes *D*₁ and *D*₂, while *Gaz* indicates the 500 liter gas holder floating on oil. The nitrogen may

be admitted at the required pressure into the condensation spiral CS from the cylinder RN through a final drying tube D_3 containing phosphoric anhydride, as well as directly from the compressor. The spiral is placed in a vacuumglass B with a protecting cylinder A . Liquid oxygen is admitted into B through $Ox.liq$ from the oxygen circulation of the cryogenic laboratory, viz. from the condensation spiral which is cooled in the ethylene boiling flask (Comm. 14, Dec. '94). The oxygen escapes through $Ox.vap$, a wide safety tube S being connected in the ordinary way, and is compressed into the spiral by a BROTHERHOOD-compressor which is lubricated with glycerine and arranged as described in Comm. 51. It may be remarked that, with a view to the possibility of an explosion of a glycerine mist mixed with oxygen, the pressure in this operation is not raised above 80 atmospheres. (Comp. the explosion described in the Zeitsch. f. Kohlensäure Industrie 1903).

The nitrogen condenser itself has been drawn in detail on plate VII. In so far as the parts correspond — either with plate V for the cover, or with plate I of Comm. 51 for the regulation cock described there — the same letters have been used, but as some of the parts differ a little the letters have an additional accent. As in the case of the small cryostat plate V, the cover is coated internally with nickel-paper, while the upper turns of CS are protected again by a ring of paste board and nickel-paper. The condensation spiral consists in the condenser proper CS_2 and the regenerator CS_1 ; here the same principle has been applied which has been followed in the cryogenic laboratory from the first (Comp. Comm. 14 Dec. '94); the vapour of the oxygen is forced by the cylinder B''_2 which is closed at the bottom with the stopper B''_{30} to pass along the regenerator spiral. As in the ethylene boilingflask (see comm. 14 Dec. '94) the level of the liquid oxygen in the glass tube W is indicated by a cork float dr_1 with a steel capillary dr_2 to which a thin reed d_3 is fastened; the steel capillary passes through a glass tube B'_{31} .

Liquid nitrogen flows out through the fine regulatingcock h h_3 of the same kind as that through which the liquid gas is admitted into the cryostat. For the description of this cock compare Comm. 51 and 54.

It may be added that Gaz' shows the connection with the auxiliary apparatus described in Comm. 54 for operations where HgC is used, which connection make it possible for the gas to stream back to the gasholder Gaz .

V. *Arrangement of a BURCKHARDT-WEISS vacuum pump to be used with a circulation for low temperature.* The well-known excellent

vacuumpump patented by BURCKHARDT and WEISS has been first used, I think by OLSZEWSKI, for removing the large volumes of gas which rise from a bath of liquefied gas at a reduced pressure. We shall now speak of some modifications and auxiliary apparatus by means of which the perfect purity of a gas is secured in a high vacuum. A pump arranged in this way may also be introduced into circulations of costly gases. In our laboratory it has been worked very satisfactorily for many years. A diagrammatic figure of the entire BURCKHARDT-pump has been given on plate VI *Bu. Vac.*, the pump cylinder with its slide valve box, the beginning of the suction- and the delivery tubes with the auxiliary apparatus belonging to them are shown on plate VIII, where fig. 1 gives the side elevation, fig. 2 the top elevation and fig. 3 the section. The well-known working of the piston and the valve, the successive communication of the valve ports 5 and 5', each individually by means of the slide hole 2 with the suction valve port 1 or with the delivery valve port 4 and together by means of the ringshaped opening 3 may be seen without further comment from the section. The pump displaces 360 M^3 an hour, hence, when exhausting at a pressure of 2 c.m., about 10 M^3 gas, measured normally can circulate. At Leiden it is used almost exclusively with an additional vacuumpump exhausting at the compression side. It exhausts then till 2 m.M.

As a lubricant and for the airtight fittings to be described in the following pages, only bone-oil is used which after having been tested at the exhaustpump has proved to have no perceptible vapour pressure.

For the technical work ordinary ring packings are quite sufficient, I have, however, replaced them by folded packings as described in Comm. 54 Jan. '00 for the compressor and the auxiliary compressor. The leather ring of the packing is supported there as in Plate IV b_{14} by the india rubber ring b_{42} (for an exhausting packing comp. E_{12} Pl. VII fig. 3 Comm. 54). The packing cylinders have been made long enough to contain two folded packings (one for exhausting and one for compression) and a bronze tightening piece, but as a rule they only hold the packing for exhaust.

New additions are the vessels O_1 and O_2 see also plate II filled with oil (or with glycerine for those gases which cannot be used with oil); they serve to protect the packing cases of the cylinder and the slide valve box entirely from the atmosphere and also to cool the piston rod. The covers O_{10} and O_{20} protect the lubricant against dust or moisture.

For the oil holders $S_1 S_2$ we have chosen the construction explained in detail in fig 7. S_{12} is an ordinary oilpot for visible cylinder lubri-

cation in vacuo. The cover S_{128} has been tightly screwed on the hollow rod S_{1290} and presses the glass S_{1291} hermetically on to the packings. By means of the winged nut S_{123} the point is adjusted so that the oil drops regularly through the openings S_{1291} into the space S_{124} which communicates with S_{126} through S_{126} and which may be watched through the glass windows in S_{124} . For our purpose the oil holder S_{12} is placed on a stout tube S_{13} onto which by means of india rubber rings and tightening bands the glass cylinder S_{11} is fixed on a copper bottom, soldered to S_{13} . The glass cylinder is filled with oil and covered with a lid S_{15} . By means of S_{122} new oil can be admitted from the reserve vessel into the lubrication vessel. In this way the air is sufficiently prevented from entering the lubrication apparatus.

Lastly, between the exhaust tube z and the compression tube p a safety valve has been placed, which prevents the pressure on the compression side from rising above a certain height (usually $\frac{1}{4}$ atmosphere). Hence it is possible to let the pump work on and to open and shut the cocks as the work requires. The noise of the safety valve gives warning that the cocks have not been properly used. In any case no difficulty is to be feared if the possible output of the pump might diminish in any way in relation to the intake. Fig. 4 shows a diagram of this connection, some of the parts being drawn to proportion; fig. 6 shows a section of the safety valve case itself.

The side tube p_1 is connected by a joint K with the tube v_1 which opens into the space below the safety valve. The space above the safety valve communicates with the exhaust tube through the side tube z_1 . The broad valve v_3 is coated at the bottom with an india rubber sheet which presses against the narrow rim v_4 . The spring v_5 is stretched with the key v_7 while the plate v_8 with the nut v_{61} and packing is tightly screwed on to the rim v_{10} . The packing cylinder v_{11} , like the packing just mentioned is kept under oil; a cover v_{12} above it protects it from dust.

The connection K between the tubes p_1 and v_1 could not be brought about with flanges or with screw joints without causing tension in the tubes. Therefore it was made in the following manner as shown by fig. 5. A widened piece k_1 is soldered on p_1 , v_1 fitting into this piece. The india rubber connection k_2 is kept in oil; for this purpose a rim k_3 was used which was soldered on to p_1 and a rim k_4 which was soldered on to z_1 . Over these rims a wide piece of tubing k_5 is drawn which is fastened to k_3 and k_4 by means of india rubber rings k_6 k_7 and tightening bands, and forms together with these an oilreservoir.

Besides being connected through the safety valve case and the above mentioned connection, the compression tube and the exhaust tube are also connected (comp. again the diagrammatic fig. 4, as an explanation of figs. 1, 2, 3) by the cocks r_1, r_2, r_3, r_4 and may be connected with an airpump l , an indicator i and a vacuummanometer m . The use made of this auxiliary apparatus in regular working or in preparing, mounting, testing, drying and exhausting the pump, requires no further explanation. As a matter of course, the pump is not introduced into a circulation unless it has worked for a long time with the exhaust- and compression sides closed and no change has been found in the vacuum.

I further remark that the principle of an oilconnection as illustrated by fig. 5 may be profitably applied when wide tubes have to be connected, which have neither flanges nor nuts and joints or in cases where it is not advisable to make these contrivances. The method then to be followed is illustrated by fig. 8 where K'_1, K'_3 and K'_4 are loose pieces slid on the tubes b_1 and b_2 , which we want to connect. A good fit is obtained by means of the india rubber rings $K'_{21}, K'_{22}, K'_3, K'_7, K'_6$, under brass tightening bands. K'_{91} and K'_{92} serve to admit and to run out the oil. In this way one always succeeds in making within a short time an airtight fit. For the connection of the pump tubes to the conduit at f_1 and f_2 (comp fig. 1) this method has been used in a manner which will be clear from the figure.

Physics. — Communication n°. 84 from the Physical Laboratory at Leiden "*Isotherms of diatomic gases and their binary mixtures. V. An accurate volumenometer and mixing apparatus.*" (By H. KAMERLINGH ONNES and H. H. F. HYNDMAN).

§ 19. *A compression tube of larger dimensions.* In § 6 of Comm. n°. 69 March '01 we have explained that the apparatus described in §§ 3 and 4 hardly gave the accuracy required in the determinations of density, if the total quantity of compressed gas was smaller than 5 cc. Since, however, at most 600 cc. of gas under normal conditions is available in this apparatus it is not suitable for densities of more than 120 times the normal.

On Pl. I a compression tube is shown which has about three liters capacity and hence which is suitable for measurements up to densities of some 500 times the normal and with at least the same accuracy as the above. The drawing is, as usual, schematic in

the connections but the individual parts are drawn to scale, it can be compared with Pl. I of Comm. n°. 69. For those parts which correspond the same letters are retained, where an alteration has been made the letters are accented, while new parts are characterised by new letters. A detailed description is hence unnecessary, but it may be noted that the screw head a_4 is changed, that a closed nut screwed on at c_{121} has been added by which the pressure can be suddenly released if necessary, and that a cock c_{15} has been introduced, to enable the level glass to be shut off if required.

The compression tube A'_1 is designed for use in the first place with piezometers of the kind described in § 2 but of larger dimensions. The use of this tube A'_1 is then the same as the original A_1 (comp. §§ 3 and 4) and it may be introduced directly in place of this into the system shown on Pl. I of Comm. n°. 69.

In the second place this compression tube serves to hold glass tubes with a stem b_4 — b_6 (cf. Pl. II fig. 2 Comm. n°. 69) onto which other apparatus can be screwed in place of the simple nut and capillary shown there. In Pl. I fig. 2 is shown a three way cock with two steel capillaries g_1' and g_1'' which is employed as follows.

One of the capillaries g_1' is connected directly with the small measuring piezometer of the type of f fig. 2 Pl. II Comm. N°. 69 the other g_1'' with a volumenometer, so that when k_{110} is shut and k_{130} and k_{120} are open a known quantity of gas can be brought into the compression cylinder from the volumenometer. On the other hand when k_{110} is open and k_{130} shut this gas can be compressed into the piezometer where the temperature and pressure are measured as before. The large glass tube with stem and the piezometerreservoir, form in this way a piezometer of variable volume (constant quantity) and the difference with the former method consists in the measurement of the normal volume in a volumenometer instead of in the piezometer itself. The volume of the large glass tube in this method is not required to any high accuracy and the small u tube at the bottom may be omitted (g_1 Comm. n°. 50 Pl. I fig. 4 June '99 and b_2 Comm. n°. 69 Pl. II March '01). The accuracy is now really that obtainable with the volumenometer (cf. § 20) in so far as the determination of the normal volume is concerned. The spaces k_{001} , k_{130} , k_{120} of the small three way steel cock must be also accurately calibrated. Care is taken also that the pins really shut properly into the sockets which makes the whole absolutely trustworthy up to at 100 At.

Although we wish to confine ourselves to the method of variable volume (constant mass) a second measurement with the volumenometer

meter is required, in the same manner as would be necessary if we employed the method of constant volume. For, we have already mentioned in § 1. that this compression apparatus is suitable for this method. The measurement is made by shutting k_{110} under known pressure and allowing the compressed gas to expand through the capillaries g_1'' and g_1' into the volumenometer and reading as before. This second volumetric measurement, with its necessary corrections, gives the determination of the normal volume after the measurements at high pressure and compares with the second normal volume determination of the original method.

§ 20. *An accurate volumenometer.* The volumenometer mentioned above in § 19 was designed to give isothermal measurements of an accuracy of $\frac{1}{10000}$ up to 60 Ats pressure. Hence the same accuracy was desired as with the standard piezometers of Comm. n° 50 June '99, while at the same time the determination of the deviations from BOYLE'S law at ordinary pressures was kept in view. The most analogous apparatus is that employed by LEDUC; that of WITKOWSKI, who has used a form more closely analogous with ours, does not appear to have been designed for high accuracy.

The measuring vessel E_b (Pl. II fig. 1 and more in detail fig. 2) where the gas is shut off by mercury entering through $E_{b_{01}}$ consists principally of 5 bulbs E_{b_1} such of 250 cc. and a smaller bulb E_{b_2} of 25 cc. capacity. These are separated by short really cylindrical portions $E_{b_2} \dots E_{b_5}$, on each of which there is a mark, near to which the mercury meniscus is brought for the measurements.

At the lower end of the measuring vessel is a contrivance after the scheme of Comm. n°. 27, for catching any dust or stray gas which may perchance come from the rubber tube at Cl_1 Pl. II fig. 2. At the upper end the vessel terminates in a capillary tube $E_{b_{90}}$ which is divided almost immediately into two $E_{b_{91}}$ and $E_{b_{92}}$. One of them is terminated near the apparatus by a cock r_3 . The other ends in a glass or steel capillary terminated also by a cock. On Pl. II fig. 2 e. g. the volumenometer is connected to the mixing apparatus F by a capillary tube soldered on to it after it has been mounted in E_a by the cock r_4 . At $E_{b_{93}}$ (Pl. II fig. 1) e. g. r_9 the steel capillary g_1'' proceeding from the three way cock mentioned in § 19 may be connected. The small bulb E_{b_2} is calibrated by mercury at the same time as the larger and serves to determine the small volumes above $E_{b_{92}}$.

To keep the temperature of the gas constant and uniform the measuring vessel is firmly fixed to the bottom of the copper case E_{a0} ,

through which water at constant temperature flows from the thermostat described in Comm. n^o. 70 III May 01 (see E_{a_2} on Pl. II, fig. 1). Uniformity of temperature is also assisted by the movement of the stirrer on to which the thermometer Th is fixed.

The ring E_{a_0} together with the bottom plate is soldered to the case E_{a_0} and is large enough for the measuring vessel to be put through it. The closing plate E_c is made fast to the measuring vessel and is so arranged, that it can easily be made watertight and that it can bear the weight of the whole mass of mercury when the tube is full without any danger to the glass as long at least as it is not displaced from its vertical position. The closing plate with flange and packing is pressed against the ring E_{a_3} at the bottom of E_a by the screw E_{c_1} . The different parts will be seen by an inspection of Pl. II fig. 1. E_{c_2} the ring and packing, made large enough to be brought over the measuring vessel, E_{c_4} and E_{c_5} round copper plates provided with a thread and cut out at E_{c_4} and E_{c_5} enough to pass over the tube E_{b_0} , so that they can be put on from the side and made fast together by the screws E_{c_3} ; together they form the closing plate which is screwed into E_{c_2} ; E_{f_1} and E_{f_2} the halves from a round vulcanite plate which rest on the ring E_{c_3} with bottom E_{c_4} and support the enlargement $E_{b_{01}}$. E_{f_2} and E_{f_3} the two halves of a rubber plate which are united by rubber solution and pressed into the ring E_{c_2} to make the whole watertight.

When the closing plate has been made fast perpendicularly to the measuring glass and has been screwed against the lower rim of E_a , the two parts of the conical top E_m are brought together into place and the measuring glass centered and held fast by the cork E_k . The whole waterbath is then brought into as vertical a position as possible.

There are windows in the case E_a which enable the tube to be lighted and read. These are formed by thin pieces of plate glass held between stout brass frames E_{h_1} and E_{h_2} one of which is soldered to the wall of E_a . The screws E_{h_3} enable the plate to be equally pressed against the rubber packing E_{h_5} and the glass. It is quite necessary to have the case completely tight, which was here obtained, to prevent the felt in which E_a is packed from becoming wet, and hence from an irregular loss of temperature.

In spite of the verticality of the entire case the glasses require to be tested with a contact spirit level, in order that the necessary correction to the cathetometer reading may be made.

To determine the volume of an enclosed quantity of gas the position of the meniscus is not read with reference to the marks on the glass

tubes, but on finer lines etched on to small glass plates E_{91} — E_{97} , provided with connections E_{90} and screws E_{91} to fix them to the cylindrical portions of the measuring vessel. By a proper arrangement of these the meniscus and the lines can be sharply seen over the whole length of the case.

The measuring vessel is calibrated by temporarily blowing on, at the lower end, a small glass cock with a fine point (cf. Comm. N°. 70. IV. May '01). The mercury is introduced through this in the carefully exhausted apparatus and the menisci are then read in the manner described above for the measurements and with the same precautions as to lighting and temperature. The mercury drawn off at the cock is weighed. As before the readings are made on the glass plates but in order that the calibration shall not be lost if these have to be removed, they are also compared with the lines on the cylindrical tubes. This would be necessary if the tube had to be removed cleaned and dried after the method of Comm. N°. 27, but usually it is sufficient to suck up the various liquids and to dry by repeated evacuation admission of dry air through r_6 and r_1 of Pl. II fig. 2.

The measuring vessel can be completely shut off from the mercury reservoir, see Pl. II fig. 2 or the manometer by the clamp Cl_1 . All these connections are carefully cleaned good thickwalled black rubber tubes, which are strengthened by wrapping them spirally in strong tape. The mercury meniscus (cf Comm. N°. 67 Dec. '00 for what is here implied) remains quite clean after a series of measurements, if only dry gas is admitted to the volumenometer (this is only true when the gas has no action on the fat of the cocks and joints). The small changes in the position of the meniscus to bring it to the required position are made by manipulating the clamp Cl_3 and the reservoir. During the measurements this clamp is always closed.

The pressure of the gas in the volumenometer is given by the height of the mercury in the manometer tube when Cl_1 is quite open. This is itself connected to a barometer and a reservoir at constant temperature by airtight connections in the manner of Comm. N°. 60 June '00 and the same precautions are taken to ensure accuracy in the temperature determinations of these two mercury columns. The volumenometer meniscus and etched lines, manometer, barometer and standardscale (cf Comm. N°. 60) are so placed that they can be read without altering the telescopes of the cathetometer.

The menisci of the barometer and manometer are read as described before, that of the volumenometer by the help of a brass plate with a 2 mm. slit in it, which is brought with a glow lamp to the same level as a meniscus and gives good definition.

In order that the required accuracy may be obtained it is necessary that the pressure shall not fall below 0,5 Atm.

To determine the theoretical normal volume measurements are made at two or if possible at three positions with the same quantity of gas. Whenever the third virial coefficient C (cf Comm. N°. 71 June '01 and N°. 74)¹⁾ does not come into account at the pressures considered and to the accuracy required, the same value of the coefficient B must be found by a combination of any two of the three measurements. This gives directly the deviations from the law of BOYLE and hence the theoretical normal volume.

§ 21. *The mixing apparatus.* On Pl. II fig. 2 the volumenometer described in § 20 is shown connected with other apparatus for the preparation of accurate mixtures of gases and for the investigation of their compressibility.

The drawings do not require much explanation. The mixing vessel F and the reservoir G have about 2 liters capacity. G is provided with a three way cock and is particularly useful when a number of mixtures are required with a small proportion of one component which can be contained therein.

The connecting tubes between r_5 , r_8 , r_9 and from E to r_6 are narrow so that the uncertainty of their temperature may have no influence on the accuracy of the measurements, the other tubes are large enough to allow free connection between the various parts and the pump and to help rapid exhaustion.

When a mixture of given composition is required, and the mercury stands above the closed clamps Cl_1 , Cl_2 , Cl_3 , Cl_4 , the whole apparatus is pumped out through r_1 and is filled through r_4 , while r_8 is shut, from say the gas apparatus connected to r_2 , after being washed out with this gas.

Then r_2 is shut and r_7 so turned that the gas is shut up in G while F is brought into connection with the pump through r_4 . The cocks r_8 , r_5 and r_6 are then opened and E and F and the connections pumped out again. By raising Kr and opening Cl_2 widely and Cl_1 (to prevent air entering from M) only partially the mercury is caused to enter E and to fill first E_{b03} without enclosing any gas, then E_b up to the required position, when Cl_1 is shut. The space between r_5 , r_2 , r_3 , r_1 is repeatedly washed out by a small quantity of gas from G through the cock r_4 , from here also gas is

¹⁾ Livre jubilaire dédié à J. BOSSCHA; Archives Néerlandaises, Ser. II. T. VI. p. 874—888. 1901.

brought into E and the whole pumped to a good vacuum. The required quantity of gas can then be brought into E through r_4 and r_5 . The volume, temperature and pressure of the gas in E_a shut off by r_5 and r_6 are then accurately measured and when r_6 is opened nearly the whole of this can be brought over into F . The remaining portion in $E_{b_{90}}$ and $E_{b_{92}}$ is then measured by expanding to $E_{b_{82}}$ or $E_{b_{81}}$ and Cl_1 is again closed so that E can be again evacuated. The second gas is then brought directly into the volumenometer from r_3 and the volume measured in the same manner.

When this is finished r_6 is again opened and the second component in E mixed with the first in F where it stands for some time. The admixture of the total quantity is completed by drawing the combined gases several times backwards and forwards between the two vessels. The mixture is then preserved in F and as much as may be necessary is driven into E_b or through r_5 into other apparatus for measurements on the compressibility.

(April 24, 1903).

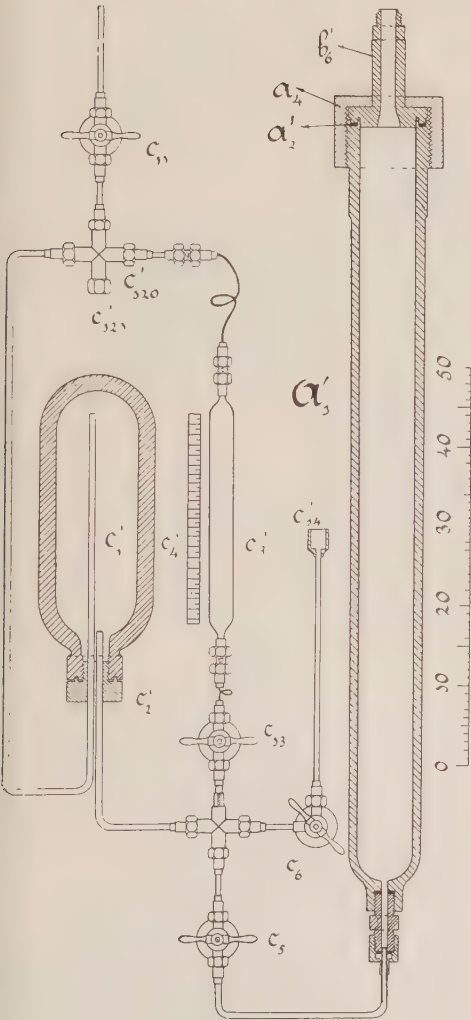


Fig. 1.

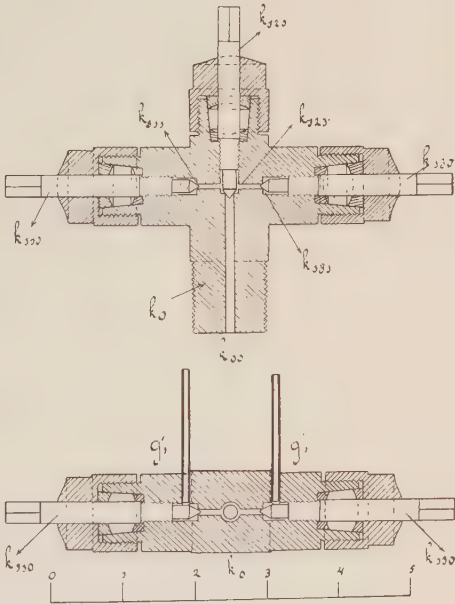


Fig. 2.

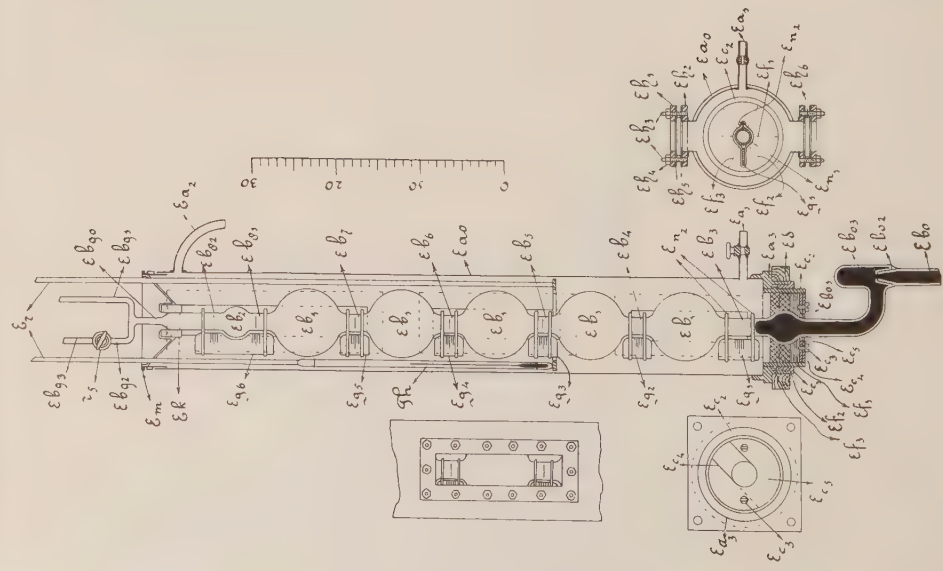


Fig. 1.

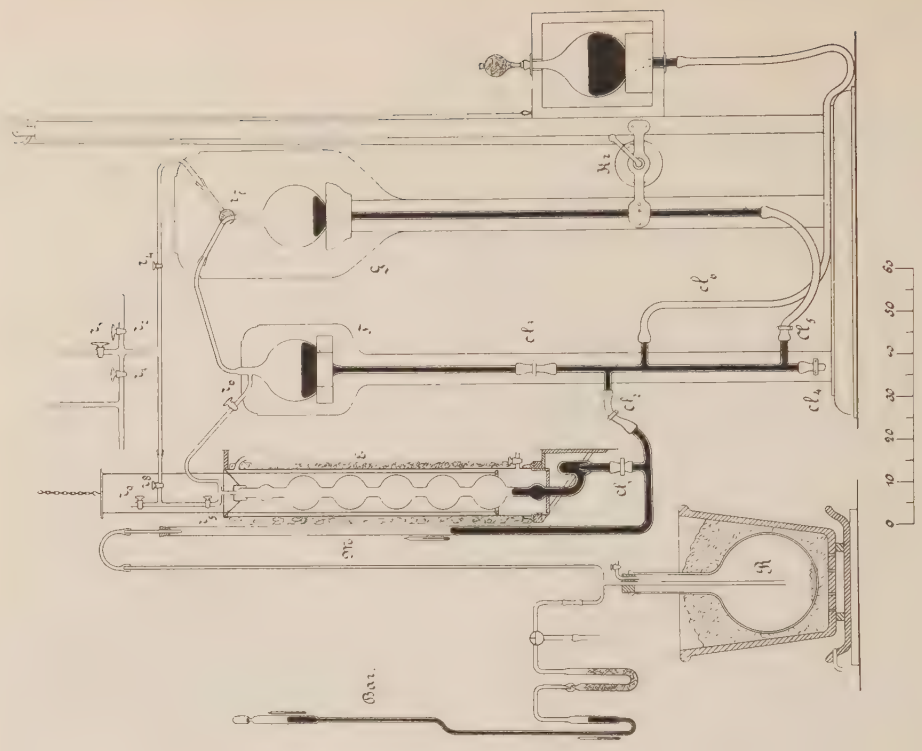


Fig. 2.

KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN
TE AMSTERDAM.

PROCEEDINGS OF THE MEETING

of Friday April 24, 1903.

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H. A. LORENTZ: "On the emission and absorption by metals of rays of heat of great wavelengths". p. 666.

G. VAN ITTERSON JR.: "The decomposition of cellulose by aërobic micro-organisms". (Communicated by Prof. M. W. BEIJERINCK), p. 685, (with one plate).

The following papers were read:

Chemistry. — "*Dissociation in and crystallisation from a solid solution*". By Prof. C. A. LOBRY DE BRUYN and Mr. C. L. JUNGUS.

(Communicated in the meeting of March 28, 1903).

It is no longer necessary to be reminded of the analogy between liquid and solid solutions but it is still a matter of importance to trace and investigate new instances of the similarity of the two solutions. For this reason attention may be called to the following phenomena and observations.

The new phenomena relate to the interesting intramolecular rearrangement discovered by CIAMICIAN and SILBER ¹⁾ in which solid or

¹⁾ Ber. 34. 2040 (1901).

dissolved o-nitrobenzaldehyde is converted, under the influence of the blue rays of sunlight ¹⁾ into o-nitrosobenzoic acid:



and where consequently an oxygen atom of the nitrogroup migrates to the neighbouring aldehyde group and oxidises the same to carboxyl. CIAMICIAN and SILBER have investigated this reaction more closely, principally with solutions in different liquids; as regards the transformation taking place in the solid condition, in which we happen to be particularly interested, they merely say: „dass die Krystalle nach und nach ihre lichtgelbe Farbe verlieren, undurchsichtig, grünlich und schliesslich weiss werden”.

The said changes in colour, the occurrence of the green coloration and the subsequent turning white render the phenomenon precisely significant for the knowledge of the properties of solid solutions. This will become evident when we think of the general and very interesting property of the organic nitrosoderivatives to suffer polymerisation and become colourless when in a solid condition; in solution, however, they are unimolecular and coloured (generally blue or green). This behaviour is quite comparable to that of nitric peroxide. In a certain number of cases the depolymerisation has been traced by cryoscopic means, as it often takes place very slowly: the lowering of the freezing point then gradually becomes greater while the colour becomes more and more intense. In this way it has been ascertained that in the colourless solid nitroso-compound two molecules have become united showing that an intense colour must be attributed to the single molecules. The same happens with NO_2 (the nitroso-compound of oxygen) which has an intense colour, whilst its polymerisation product N_2O_4 is colourless.

After these remarks it is not difficult to see in what manner the transformation of solid o-nitrobenzaldehyde into solid o-nitrosobenzoic acid must be conceived. The displacement commences as soon as the crystal is exposed to sunlight; after about 15 minutes a faint green tinge is perceptible which gradually deepens; the nitrosobenzoic acid, which is formed from and in the solvent, first remains in solid solution and, to judge from the green colour, in the unimolecular condition. On continuing the exposure to sunlight the colour becomes more intense, until finally the saturation point is reached; the outer

¹⁾ We have ascertained that an elevation of temperature does not cause the displacement.

layers of the crystal then become dull and a lighter green, the nitrosobenzoic acid, which crystallises out, is now however white and consequently bimolecular¹⁾; finally the surface of the crystal becomes quite white and opaque. The process then apparently comes to a standstill because the sunlight cannot any longer penetrate the interior of the crystal or only in an insufficient degree. In this case the interior of a sufficiently big crystal still contains a green transparent nucleus.

The titration of five different specimens has given the following result:

After $2\frac{1}{2}$ day about 3 % of nitrosobenzoic acid.

"	6 $\frac{1}{2}$	"	"	5	"	"
"	10	"	"	11	"	"
"	15	"	"	15	"	"
"	34	"	"	24	"	"

The surfaces of the last crystals had turned quite white.

Conclusions as to the velocity of transformation cannot of course be drawn from these figures, as on the one hand the source of light varied too much in intensity, whilst on the other hand the crystals were of a different thickness.

It was considered of importance to try and determine the maximum solubility of o-nitrosobenzoic acid in o-nitrobenzaldehyde. From the surface of those green crystals, which commenced to deposit the white acid, the latter was therefore as far as possible removed by mechanical means. By titration 2.6 % of nitrosobenzoic acid was then found; if now we may assume that the concentration of the acid inside the crystal is not smaller than that at the surface the saturated solid solution contains about 2.6 mols. of acid per 100 mols.

Another conclusion may still be drawn from the above, namely that o-nitrosobenzaldehyde is capable of forming mixed crystals with 2.6 mols. of o-nitrosobenzoic acid; whether these two substances are isomorphous is not known as the system of crystallisation of nitrosobenzoic acid has not been determined. Very probably they are not isomorphous as otherwise the power to form mixed crystals would occur over a larger interval or even for all proportions.

¹⁾ It has not been possible to ascertain, by the ordinary means at disposal, not even by the highest possible enlargement, that the o-nitrosobenzoic acid formed is crystalline. This cannot be a matter of surprise if we consider that the separation of the acid proceeds very rapidly and that the diffusion in solid solution is particularly slow. Still we may speak here of crystallisation as the separated substance, in contrast to amorphous compounds, exhibits definite physical constants (fixed melting point, solubility etc.).

By determining the meltingpoint line of the system of the two substances (the aldehyde melts at 45° , the acid is decomposed at about 200°) the point up to which they are still capable of forming mixed crystals may perhaps be determined more accurately. It is not improbable that in the intramolecular rearrangements of other solid substances solid solutions may also be formed; if possible this will be further investigated.

Chemistry. — "*The transformation of diphenyliodonium iodide and chloride and its velocity*". By Mr. E. H. BÜCHNER. (Communicated by Prof. C. A. LOBRY DE BRUYN).

(Communicated in the meeting of March 28 1903).

It is about 10 years ago that VICTOR MEYER and HARTMANN¹⁾ announced the important discovery of a new class of iodine derivatives, the iodonium bases, substances with a trivalent iodine atom, having about the same basic power as the ordinary alkalis and capable of forming salts. The simplest representative of this interesting class of substances is diphenyliodonium-hydroxide: $(C_6H_5)_2JOH$; the salts, such as the chloride or the nitrate, when dissolved in water, appeared to possess a conductive power corresponding with that of the alkali salts²⁾.

The behaviour of the halogen salts of the base, when heated, is peculiar; VICTOR MEYER and HARTMANN noticed that on fusing these salts at 175° a decomposition sets in, which spontaneously leads to a complete conversion into halogen-benzene $(C_6H_5)_2 = J-J = 2 C_6H_5J$ with strong evolution of heat.

This transformation now deserved a closer study. It may be considered as a depolymerisation but is distinguished however from many other similar reactions, not only by the great difference in character between the decomposing substance and the products of decomposition but also by the fact that the transformation is not reversible. At all events, up to the present no process is known which leads straight from iodobenzene to diphenyliodoniumiodide. In this latter respect the above mentioned reaction is distinguished from the transformation with which it has been compared namely that which tetramethylammonium iodide suffers on heating; the latter substance is readily prepared from its products of decomposition at the ordinary temperature.

¹⁾ Ber. **27**, 502, 1594. (1894).

²⁾ SULLIVAN Z. ph. Ch. **28**, 523. The salts are, therefore, not dissociated hydrolytically.

It was to be expected that the decomposition of the diphenyliodonium-salt would take place at temperatures considerably below the melting-point, and this is actually the case.

1. Beforehand, however, it was deemed desirable to study the behaviour of the iodide towards light as in the study of the velocity of transformation account had to be taken of a possibly existing sensitiveness to light¹⁾.

I have found that in the case of the iodide the transformation is caused by exposure to light²⁾; whilst it remains quite intact when kept in the dark for $2\frac{1}{2}$ months. It was to be expected that the source of the light would affect the transformation. The following results were obtained:

Electric Arc-Light:	after 1	hour	titre: 26.6% J,	converted about 14.5%.
"	"	"	$1\frac{1}{2}$ "	" 24.9 " " 20 "
Sunlight:	"	4	" "	30.0 " " 3.5 "
"	"	30	" "	13.0 " " 60 "
Auer Light:	"	170	" "	29.1 " " 6.4 "
Diffuse Daylight: a.	"	10 weeks:	24.7 " "	20.5 "
"	b.	"	20.3 " "	35 "

The decomposition of the iodide is therefore most rapidly effected by the arc-light.

2. If now the solid iodide was exposed to temperatures considerably below its meltingpoint a more or less slow conversion seemed to take place. Whereas 1% at most was decomposed at 90° after 3 hours, about 36% had disappeared at 100° after 13 hours, whilst after heating at 123° for $3\frac{1}{2}$ hours only 5% was left undecomposed. This shows that the decomposition of the solid substance already takes place even at temperatures considerably below the meltingpoint. This also applies to the solid chloride which however is more stable than the iodide.

Several series of experiments were now made with the solid iodide

¹⁾ The quantitative estimation of iodonium haloid and halogen-benzene in the presence of each other is simply done by titration with AgNO_3 ; the first when introduced into water yields one of the halogen atoms as ion whilst iodo- or chlorobenzene does not react with AgNO_3 .

For diphenyliodonium-iodide was found: according to CARIUS 62.1 and 62.1% J, calculated 62.2%; by titration 31.0 and 31.1% J. The chloride gave on titration 11.15% Cl, calculated 11.2%.

²⁾ V. MEYER states that it turns yellow on exposure to light.

at temperatures of 105—110°; the results obtained will be communicated on a future occasion.

3. It was obvious that I should try to make a closer study of the velocity of transformation of the iodide in solution. Its great insolubility, however, rendered the operation impossible; of the many solvents which were tried, pyridine proved to be the best; the solubility of the iodide was however still too small, namely only about $1\frac{1}{2}\%$.

The more soluble diphenyliodonium-chloride was better suited for the purpose; the solubility in water, although not large, proved sufficient at the temperature at which the operation took place (98—99°).

The results obtained in fifteen velocity determinations were at first very unsatisfactory and pointed to the existence of many interfering influences. The coefficients obtained on applying the formulae for unimolecular and bimolecular reactions were anything but constant and often pointed to a very irregular course. In one experiment coefficients were obtained which were many times greater than those got in another apparently quite analogous case. Sometimes the coefficients diminished equally, sometimes the reaction after proceeding for a while, suddenly ceased. After many similar negative results it at last appeared that the conversion of diphenyliodonium-chloride into chloro- and iodobenzene is influenced to an extraordinary degree by the presence of very small quantities of impurities. Very small quantities of acid retard the reaction to a remarkable extent or bring it to a standstill: the presence of traces of iodine causes a regular fall in the reaction coefficient; a little of the free base (diphenyliodonium-hydroxide) accelerates, on the other hand, the decomposition in a strong degree. The halogenbenzenes formed during the reaction appeared however to be inert.

On now using a very pure preparation free from acidity and of a pure white colour and applying the formula for reactions of the second order, coefficients were obtained which could be considered as constants. (see table p. 649).

On adding 6 cc. of $\frac{n}{25}$ HCl, the coefficient (which, moreover, was not constant) fell to about half the value obtained in experiment I while the presence of 8 cc. of $\frac{n}{25}$ $(C_6H_5)_2$ JOH increased the coefficient about 4 or 5 times ¹⁾.

1) The following experiment also may show how sensitive the transformation is to very trifling quantities of foreign substances. To a solution of the chloride ($C_0 = \frac{1}{20.2}$, $T = 99.0$), which after $3\frac{1}{2}$ hours had fallen from 30.67 AgNO₃ to 23.71, was added 39.3 milligr. of a well crystallised chloride which was coloured

I. T = 99°.1 C ₀ = 1/27.2 ¹⁾ 2.909 gr. in 250 cm ³ .			
t in hours.	ccm. AgNO ₃	K ₁	K ₂
0	22.96		
18	12.25	0.0152	1.32
20	11.87	143	1.27
22	11.12	143	1.31
24	10.87	135	1.26
25	10.50	136	1.29
28	9.94	130	1.27
30	9.42	129	1.30

II. T = 99.1 C ₀ = 1/16.8			
t	AgNO ₃	K ₁	K ₂
0	37.17		
1 1/2	33.82	0.0273	1.11
4 1/4	27.85	295	1.32
9	22.72	236	1.19
9 3/4	22.25	229	1.16

III. T = 99.0 C ₀ = 1/22.6 trace of iodine added.		
t	AgNO ₃	K ₂
0	27.75	
1 1/2 h.	25.37	1.43
3 1/2	23.00	1.33
5 1/2	22.00	1.10
11 1/2	18.37	1.00
23 1/2	15.77	0.88

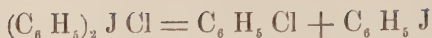
IV. T = 99.1 C ₀ = 1/22.7 25 cm ³ . n/25 HCl added to 150 cm ³ . Conc. of the HCl therefore 1/175 n.	
t	AgNO ₃
0	27.50
2 h.	27.50
4	27.12
22	26.61
neutral. with NaOH	
26	24.32
28	17.87

If, by means of the VAN 'T HOFF formula²⁾, we calculate the order of the reaction from the communicated experiments and also from a few which are not yet communicated, we find $n = 2.1, 1.9$ and 2.1 . From this, and also from the fact that in experiment I the K_2 's are constants, it follows that the transformation

somewhat yellow, but gave on analysis the theoretical number for chlorine. By this addition the titre naturally increased and came to 26.10; 2 1/2 hours later the solution did not appear to have changed (found 26.08). The somewhat coloured chloride was found to have a faint acid reaction and to give blue colour with starch solution after some time.

¹⁾ K_1 is calculated according to the formula for reactions of the first, K_2 according to that for reactions of the second order.

²⁾ Vorlesungen, I. 193.



is a bimolecular one.

Since the chloride is comparable with a salt such as KCl, it may be concluded that the transformation does not occur in the non-dissociated molecules but between the ions. This idea would agree with that propounded by WALKER and HAMBLY¹⁾ for the transformation of ammonium isocyanate in aqueous or alcoholic solution into urea, a reaction which also appeared to be a bimolecular one. WALKER and HAMBLY were enabled to support their view by showing that either ammonium- or isocyanic acid ions cause a retarding influence on the reaction investigated by them as both diminish the dissociation of ammonium isocyanate. In our case a similar behaviour of chlorine and iodonium atoms does not present itself. Hydrochloric acid has certainly a retarding influence but this is too large to be explained by a diminution of the ionisation. Then again, iodonium hydroxide has a strong accelerating power. We must, therefore, think here of a special catalyzing influence of hydrogen- and hydroxyl ions: apparently the first acts here as a retarding catalyzer, an influence of which up to the present but few instances are known. Then, if the acid is neutralised (compare expt. IV), the transformation proceeds in a regular manner whilst the chlorine ion is still present in about the same concentration.

The most probable view of the mechanism of the transformation of the iodonium haloids is therefore that the reaction takes place between two molecules.

A trace of iodine retards the transformation in an increasing degree. This investigation will be continued later on.

Organic. chem. Laboratory, University of Amsterdam.

Chemistry. — “*Nitration of symmetrical dinitroanisol.*” By Dr. J. J. BLANKSMA. (Communicated by Prof. C. A. LOBRY DE BRUYN).

(Communicated in the meeting of March 28, 1903).

In a previous communication²⁾ it has been stated that pentanitrophenol is readily formed by the action of nitric acid on symmetrical dinitrophenol whilst symmetrical dinitroanisol is attacked with difficulty by nitric acid. It seemed, however, not impossible that symmetrical dinitroanisol might still be further nitrated and this indeed appeared

¹⁾ J. Ch. Soc. **67**. 746 (1895).

²⁾ Proc. Royal Acad. 25 Jan. 1902.

to be the case. If symmetrical dinitroanisol is treated for two hours on the waterbath with a mixture of HNO_3 (density 1.44) and sulphuric acid, trinitroanisol is formed m. p. 104° . The nitrogroup introduced into this substance is mobile and easily replaced by OH , OCH_3 , NH_2 , NHCH_3 etc. If the NO_2 group is replaced by OH dinitroguaiacol is formed m. p. 121° . By treatment with alcoholic methylamine, methyl-amido-dinitroanisol is formed m. p. 168° , which is converted by nitric acid of 1.52 sp. gr. into oxymethyl-dinitrophenyl-methylnitramine m. p. 118° already obtained by GRIMAUD and LEFÈVRE ¹⁾ by nitration of dimethyl-orthoanisidine. This goes to prove that the nitrogroup in regard to the OCH_3 -group has been introduced into the ortho place and that, therefore, the constitution of trinitroanisol is represented by $\text{C}_6\text{H}_2\text{OCH}_3(\text{NO}_2)_3$. 1. 2. 3. 5.

If trinitroanisol is treated with a solution of NaOCH_3 in methyl alcohol the NO_2 group 2 is replaced by OCH_3 and the dimethylether of dinitropyrocatechine is formed, m. p. 101° . Treatment with alcoholic ammonia yields dinitroanisidine $\text{C}_6\text{H}_2(\text{OCH}_3)\text{NH}_2(\text{NO}_2)_2$ 1. 2. 3. 5, m. p. 174° ; with aniline and aethylamine are formed compounds melting respectively at 155° and 123° .

If trinitroanisol is nitrated with a mixture of nitric acid of 1.52 sp. gr. and sulphuric acid a tetranitroanisol is formed m. p. 154° . On treatment with 2 mols. of NaOCH_3 , this substance is converted into crystals which melt at 165° and assume a purple-brown color when exposed to light.

Analysis shows that two NO_2 groups are replaced by OCH_3 . LORING JACKSON ²⁾ by treating symmetrical tribromodinitrobenzene with 3 mols. of NaOCH_3 has prepared a compound with the same properties as the above mentioned; he however considered that he had obtained the dimethylether of dinitroresorcinol. The latter substance melts however, according to FREYSS ³⁾ and MELDOLA ⁴⁾ at 154° , whilst MEERUM TERWOGT ⁵⁾ and I have found 157° . It is therefore very probable that LORING JACKSON has been dealing with the trimethylether of dinitrophloroglucinol as, on treating symmetrical tribromodinitrobenzene with NaOC_2H_5 , all three Br -atoms may be replaced by OC_2H_5 ⁶⁾.

That the compound obtained from tetranitroanisol and NaOCH_3 is really identical with that from symmetrical tribromodinitrobenzene

¹⁾ Compt. Rend. **112**. 727.

²⁾ Amer. Chem. Journ. **13**. 180.

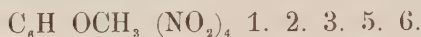
³⁾ Centr. Blatt. 1901. I. 739.

⁴⁾ Proc. Chem. Soc. **17**. 131.

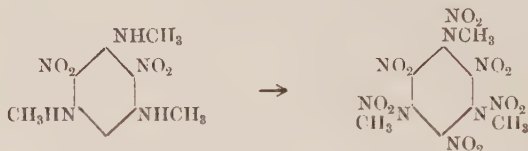
⁵⁾ Rec. **21**. 288.

⁶⁾ Amer. Chem. Journ. **21**. 512.

was shown by taking the meltingpoint of a mixture of the two substances; no lowering of the meltingpoint was noticed. It is therefore proved that from tetranitroanisol and NaOCH_3 the trimethyl-ether of dinitrophloroglucinol is obtained and consequently the constitution of the tetranitroanisol is:



If symmetrical tribromodinitrobenzene is treated in alcoholic solution with six mols. of methylamine, the three bromine atoms are readily replaced by NHCH_3 and we obtain fine orange-red needles m.p. 220° (with decomposition). When this symmetrical $\text{C}_6\text{H}(\text{NO}_2)_2 (\text{NHCH}_3)_3$ is dissolved in nitric acid of 1.52 sp. gr. and then diluted with water a fine white crystalline powder is obtained which, when dissolved in glacial acetic acid, deposits small beautiful white needles, which explode between 200° and 203° , sometimes causing a flame. From the analysis it appears that this is the symmetrical trinitrophenyltrimethyltrinitramine.



Geology. — “*Two New Mid-Cambrian Erratic-Blocks from the Dutch Diluvium*”. By J. H. BONNEMA at Leeuwarden. (Communicated by Prof. J. W. MOLL).

I. When I had been appointed assistant at the Geological-Mineralogic Institute at Groningen, I was charged with the task of determining the fossils that are found in the collection of Groningen sedimentary erratic-blocks. If we succeed in this with a fossil, we can as a rule more or less accurately, for the erratic-block in which it occurs, fix the age of the layer of which it formerly formed part; at the same time it may be found out whether suchlike stone is still known as firm rock, — and whether the same kinds of erratic-blocks have been met with in any other places.

With many pieces I succeeded, but with a not inconsiderable number I failed, owing to various causes. To the latter division belonged i. a. two small pieces of lime-stone, the largest dimensions

of which are about 4 centimetres. They originally made part of one erratic-block, which was found when the ramparts near one of the former Groningen gates (Boteringepoort) were dug off. One of the pieces still shows a part of the original surface possessing distinct glacierscratches.

From the pieces preserved it may be concluded that this erratic-block consisted of green-grey, rather compact, marly lime-stone, in which with a magnifying glass many little grey grains and here and there little dark-green lustrous Glauconite-grains may be distinguished. I observed one single Pyrite-crystal. At the surface it had, to a depth of about 1 centimetre, become more or less yellow, under the influence of corrosion.

The part preserved also shows that through this erratic-block ran a layer that was rich in Trilobites-remains. For the greater part the transverse sections of them are visible. In one piece, however, some remains are partly or entirely exposed to view. A mid-shell is the most important of them.

This mid-shell, across which run various flaws, and which consequently is not likely to have entirely retained its original shape, is lengthwise rather strongly vaulted and has a length of 12 millimetres, its breadth amounting to about 14 millimetres. It is almost everywhere the same, the lines that connect the beginning and the termination of the facial suture, running almost parallel to the longitudinal axis. The front-edge is regularly curved. The occipital-furrow is shallow, especially on the glabella. The length of the rather broad glabella is about $\frac{3}{4}$ of that of the mid-shell. It is tongue-shaped and bounded by shallow dorsal furrows. The latter first run nearly parallel to each other and then turn to the centre, where they meet. Lateral furrows are not to be distinguished on the glabella. That part of the mid-shell which lies in front of the glabella, slants down rather quickly. The parts on either side slant down more slowly.

As to the sculpture, along the front-edge of the mid-shell, parallel to it, run fine stripes. The shell moreover shows all over, very near each other, fine pricked points. The colour of the shell is partly black, partly yellow-grey (cream-coloured).

In spite of repeated efforts I had never before succeeded in discovering what species of Trilobites this mid-shell came from. This summer, however, I was more fortunate. On my journey to Oeland it chanced that near the hospital at Borgholm a pit was being dug and that, while doing this, people had penetrated as far as the layer with *Paradoxides Oelandicus* Sjögren. The stone that had been produced from the pit, was still present. It consisted of greenish marl-slate,

which had entirely fallen asunder, and of rather large lime-concretions. This clashes with LINNARSSON'S ¹⁾ opinion, that at Borgholm this layer should consist of marl-slate only, which opinion was afterward made use of by ROEMER ²⁾ and REMELÉ ³⁾.

In the said lime-concretions I found, besides some remains of *Paradoxides Oelandicus* Sjögren and a couple of nearly complete specimens of *Ellipsocephalus Polytomus* LINNARSSON, countless mid-shells of the latter species of Trilobites.

Here was confirmed the opinion of LINNARSSON ⁴⁾ that the absence of stripes on the front-edge of the mid-shells, and that of the pricked points, on the scale of the *Ellipsocephalus*-species occurring at Borgholm, by which this species was said especially to differ from the Stora Frö-species, must be attributed to the circumstance that his Borgholm material came from marl-slate, and that of Stora Frö from lime-stone. The stripes and the pricked points are remarkably distinct in the mid-shells I gathered from the lime-concretions at Borgholm. Consequently there is no reason any more for not ranging the *Ellipsocephalus*-remains of Stora Frö under the head: *Ellipsocephalus Polytomus* LINNARSSON, the difference in size only not sufficing to maintain the contrary.

One of the lime-concretions contained a layer that was peculiarly rich in mid-shells of *Ellipsocephalus Polytomus*. While breaking this concretion to pieces, I was immediately reminded of my Groningen erratic-block; and now that I have compared the latter with the pieces I brought from Borgholm, I know that they are exactly alike. In both the stone is the same, except that the Groningen piece has a yellow tint, which must be attributed to the influence of corrosion. The mid-shells of *Ellipsocephalus Polytomus*, occurring in both, also resemble each other, in colour as well as in their numerous flaws.

Consequently it may with perfect certainty be declared that the erratic-block mentioned above has the same age as the layer with *Paradoxides Oelandicus* Sjögren (the oldest of the Mid-Cambrian), and that a corresponding kind of stone is still found at Borgholm in Oeland. It is probably also met with at Stora Frö in the same island. I cannot say so for certain, however, as I did not go there and so do not possess any limestone from that place, which might be used for comparison.

¹⁾ LINNARSSON. Om Faunan i lagren med *Paradoxides Oelandicus*. Geol. Förenings i Stockholm Föreläsningar, Bd. 3. pag. 354.

²⁾ ROEMER. *Lethaea erratica*. pag. 37.

³⁾ REMELÉ. *Zeitschr. d. deutsch. geol. Gesellschaft*. Bd. 33. 1881, pag. 183, 701.

⁴⁾ LINNARSSON. *Loc. cit.* pag. 364.

This is the first time that mention is made of such an erratic-block from the Dutch diluvium. Many of the kind, with remains of *Ellipsocephalus Polytomus* or of other fossils, occurring in Oeland in the layer with *Paradoxides Oelandicus*, have already been found in the German diluvium. The first of them was mentioned by DAMES¹⁾ and comes from Rixdorf near Berlin. A few years after, REMELÉ²⁾ described two such erratic-blocks from the neighbourhood of Eberswalde. Later on, ROEMER³⁾ made mention of two erratic-blocks of the same age. One of them comes from Rostock and bears much resemblance, according to the description, to the Groningen piece. This cannot with so much certainty be said of the second block, which was found at Bromberg and does not seem to be greenish. In Sleswick-Holstein, too, corresponding erratic-blocks seem to have been found, as STOLLEY⁴⁾ writes about „grünliche Kalkgeschiebe der Oelandicus-Zone”.

This erratic-block also confirms my supposition formerly⁵⁾ mentioned, that in the Hondsrug occur more sedimentary erratic-blocks with a West-Baltic character, than was formerly generally supposed.

II. For some time already I have had in my collection several pieces of an erratic-block consisting of limestone that has been tinted dark-grey, even almost black, by bitumen. It was found in the loam-pit near Hemelum. Its calcium-carbonate having for the greater part crystallized, this limestone approaches antracinite. Some nests of little pyrite-crystals and a small phosphorite-nodule are found in the stone.

For a long time the only fossil that was exposed to sight was (with the exception of a few unimportant remains, probably of a *Paradoxides*) what I supposed to be the internal cast of the inside of a piece of Trilobite-shell. Its largest dimension amounts to 9 millimetres. This internal cast is almost oval, and strongly vaulted. The top-part finishes in a bow. On the convex side of this bow it is steeper than on the concave one. In front, on the least steep part, is a frame in relief, soon turning round the most elevated point and then continuing on the steepest part, where it becomes tinier and tinier. Towards either side springs from this frame a net-work of

¹⁾ DAMES, Zeitschr. d. deutsch. geol. Gesellschaft. Bd. 31. 1879. pag. 795.

²⁾ REMELÉ, Zeitschr. d. deutsch. geol. Gesellschaft. Bd. 33, 1881. pag. 181, 700.

³⁾ ROEMER, Lethaea erratica, pag. 26.

⁴⁾ STOLLEY, Die Cambrischen und Silurischen Geschiebe Schleswig-Holsteins und der benachbarten Gebiete, 1895. Bd. I, Heft 1, pag. 40.

⁵⁾ BONNEMA. "Cambrian erratic-blocs at HEMELUM in the South-west of Frisia." These Proc. 1902, p. 142.

suchlike ones. This net-work is very distinct on the less steep part, not so distinct on the other, where it is scarcely to be seen with a magnifying glass. Moreover there are on this internal cast round elevations.

It being quite impossible for me to find what species of Trilobites this off-print came from, the exact age of this erratic-block could not be fixed. The nature of the stone made it likely to be Cambrian, and that, too, Mid-Cambrian, because of the suppositional Paradoxides-remains.

When, however, a few weeks ago, my friend dr. GRÖNWALL from Copenhagen, the author of "Bornholms Paradoxideslag og deres Fauna" (Danmarks geologiske Undersøgelse II Række No. 13.) took a view of my collection of erratic-blocks, he recognized in the said off-print that of a right cheek of *Conocoryphe Exsulans* Linnr.¹⁾ Herewith the age of this erratic-block was already exactly determined, for the occurrence of these Trilobites-remains is characteristic of the lower part of the layers with *Paradoxides Tessini* Brongn.

This division consists, in Schonen, in Bornholm and (according to an oral communication of prof. MØBERG) to the South of Mörbylänga in Oeland, of limestone, which after this Trilobite is at present mostly called *Exsulans-limestone*, whilst it ceased to be called *Coronatus-limestone*.

GRÖNWALL's opinion was brilliantly confirmed, when, on his breaking the stone further to pieces, remains of the Trilobites *Conocoryphe Impressa* Linnr.,²⁾ *Liostracus Aculeatus* Ang.³⁾ and *Solenopleura Parva* Linnr.⁴⁾ were exposed to view by him. Moreover a remnant of *Aceroteta Socialis* v. Seebach was found, which, however, also occurs in older and in younger layers, which is not the case with the Trilobites mentioned just now.

The only remnant that has been well preserved, is a mid-shell of *Conocoryphe Impressa* Linnr. It is for the greater part exposed to view. Only on the sides it is still covered by the stone; so the facial sutures are invisible. It must have belonged to a young individual, its length being only 6 millimetres. It is slightly vaulted, the glabella a little more than the other part. In front it is bounded by a flat border along the edge, which border is broadest in the middle.

1) LINNARSSON. Om. Faunan i Kalken med *Conocoryphe exsulans* (*Coronatus-Kalken*). Sveriges geologiska Undersökning. 1879. Ser. C. No. 35. pag. 15. tafl. II, fig. 21, 22.

2) LINNARSSON. loc. cit. pag. 20. tafl. II. fig. 29, 30.

3) LINNARSSON. loc. cit. pag. 11. tafl. I. fig. 12—15.

4) LINNARSSON. loc. cit. pag. 14. tafl. I. fig. 16—19, 20 ?

The occipital furrow is shallow, especially on the glabella. The neck-ring broadens towards the centre and bears a little tubercle there. The breadth of the glabella is at the back equal to its length, which is half the breadth of the mid-shell. The glabella becomes gradually narrower towards the front; in front it is rounded. On either side there are three very indistinct lateral furrows. The dorsal furrows are little developed. In front of the glabella the cheeks run almost imperceptibly into each other. On either side an oblong elevation is visible on the firm cheek, just behind the place where the dorsal furrow turns down towards the centre. It is scarcely to be observed that starting from this elevation a line-shaped one runs in the direction of the corners of the cephalon, as LINNARSSON tells us. This must certainly be attributed to the circumstance, that this mid-shell belonged to a young individual. The scale possesses no other sculpture than countless very fine impressed points, placed very close to each other.

From the properties mentioned above one may easily convince oneself that the mid-shell described comes from *Conocoryphe impressa* Linnr., and that consequently this erratic-block is a piece of *Exsulans*-limestone.

The other *Trilobites*-remains, all of them pieces of mid-shells, are too incomplete to be described in such a manner, that the species of *Trilobites* which they come from might be recognized from the description. Moreover, such a description would be more or less superfluous, as the age of this erratic-block has already been sufficiently indicated. So I think I'd better leave it and refer to the authority of Dr. GRÖNWALL with regard to the remains of the other *Trilobites* mentioned. As he was so kind as to send me some mid-shells of these *Trilobites* for comparison, I could convince myself of the correctness of his determinations.

As was mentioned above, *Exsulans*-lime is found as firm rock in Bornholm, in Schonen, and southward of Mörbylånga in Oeland. Mörbylånga does not seem to have been mentioned yet in literature in this connection; but Prof. MOBERG told me of it. In Schonen, *Exsulans*-lime is without any doubt met with as firm rock near Andrarum, Gislöf and Kwiks Esperöd. Most probably it is also found as such, according to LINNARSSON, near Fågelsång in the neighbourhood of Lund.

GRÖNWALL tells me that my erratic-block does not, petrographically, correspond with the Bornholm *Exsulans*-lime, more with that in South-East Schonen. I cannot decide whether it also resembles that which is found at Mörbylånga in Oeland.

In the Dutch diluvium an erratic-block of this kind was never

before found. They also seem to be very rare in the German diluvium. As far as I have been able to find out, they are made mention of by STOLLEY ¹⁾ only.

Mathematics. — “*An analytical expression for the greatest common divisor of two integers.*” By Prof. J. C. KLUYVER.

In this paper we propose to construct certain functions z of two real variables x and y which for positive and integer values of these variables become equal to the greatest common divisor of x and y .

A very simple solution of this problem is obtained as follows. Denote by $[u]$ the integer part of the number u and consider the arithmetical discontinuous function

$$P(u) = u - [u] - \frac{1}{2}.$$

For any integer n we have

$$P(u + n) = P(u), \quad P(n + 0) = -\frac{1}{2}, \quad P(n - 0) = +\frac{1}{2}.$$

We will take

$$P(n) = P(n - 0) = +\frac{1}{2}$$

and consequently

$$[n] = [n - 0] = n - 1.$$

Integer values of u excepted the wellknown relation

$$P(u) = -\frac{1}{2} \sum_{n=1}^{n=\infty} \frac{\sin 2\pi n u}{2\pi n}$$

holds and from it we deduce the identical equation

$$\sum_{\mu=0}^{\mu=\alpha-1} P\left(u + \frac{\mu}{\alpha}\right) = \sum_{\mu=0}^{\mu=\alpha-1} P\left(u + \frac{\mu\beta}{\alpha}\right) = P(\alpha u),$$

where α and β are relative prime integers. That the identity is still valid for integer values of u may be easily verified.

By the equation

$$z = 2 \sum_{\mu=0}^{\mu=[x]} P\left(\frac{\mu y}{x}\right) \dots \dots \dots (1)$$

a discontinuous function of the variables x and y is defined. We may regard it as a first solution of the proposed problem. For if

¹⁾ STOLLEY, loc. cit. p. 41.

x and y become integers, say $x = \alpha D$, $y = \beta D$, where α and β are prime to each other, we have

$$z = 2 \sum_{\mu=0}^{\mu=\alpha D-1} P\left(\frac{\mu y}{x}\right) = 2 D \sum_{\mu=0}^{\mu=\alpha-1} P\left(\frac{\mu}{\alpha}\right) = 2 D P(0) = D.$$

In a somewhat different form this result is found in a paper by STERN¹⁾. A whole set of functions of the required kind may be deduced in quite the same way. We only have to notice that the function

$$F_s(u) = \sum_{n=1}^{n=\infty} \frac{\cos 2 \pi n u}{n^s}, \quad (s > 1)$$

satisfies the fundamental relation

$$\sum_{\mu=0}^{\mu=\alpha-1} F_s\left(u + \frac{\mu}{\alpha}\right) = \sum_{\mu=0}^{\mu=\alpha-1} F_s\left(u + \frac{\mu\beta}{\alpha}\right) = \alpha^{1-s} F_s(\alpha u),$$

where again α and β are prime to each other.

Hence if we put

$$F_s(0) z^s = \alpha^{s-1} \sum_{\mu=0}^{\mu=\alpha-1} F_s\left(\frac{\mu y}{\alpha}\right), \quad \dots \dots \dots \quad (\text{II})$$

we get for $x = \alpha D$, $y = \beta D$

$$F_s(0) z^s = \alpha^{s-1} D^{s-1} \sum_{\mu=0}^{\mu=\alpha D-1} F_s\left(\frac{\mu\beta}{\alpha}\right) = \alpha^{s-1} D^s \sum_{\mu=0}^{\mu=\alpha-1} F_s\left(\frac{\mu\beta}{\alpha}\right) = D^s F_s(0),$$

that is

$$z = D.$$

In the functional relation (II) the term $F_s\left(\frac{\mu y}{\alpha}\right)$ is not easily evaluated; hence the series $F_s(u)$ may be suitably replaced by the latter of the two series

$$g_{2k-1}(u) = 2(-1)^k \sum_{n=1}^{n=\infty} \frac{\sin 2 \pi n u}{(2 \pi n)^{2k-1}},$$

$$g_{2k}(u) = 2(-1)^{k-1} \sum_{n=1}^{n=\infty} \frac{\cos 2 \pi n u}{(2 \pi n)^{2k}}.$$

Indeed, if we denote the Bernoullian polynomial of order m

$$\frac{u^{m+1}}{(m+1)!} - \frac{1}{2} \cdot \frac{u^m}{m!} + \frac{B_1}{2!} \cdot \frac{u^{m-1}}{(m-1)!} - \frac{B_2}{4!} \cdot \frac{u^{m-3}}{(m-3)!} + \dots,$$

by $f'_m(u)$ the series $g_m(u)$ is identical with $f''_m(u)$ for all values of u between zero and unity. Therefore, whatever may be u , the series $g_m(u)$ may be regarded as a polynomial of the m^{th} degree in

¹⁾ "Zur Theorie der Function $E(x)$," Journal f. Math., 102, p. 9.

$u = [u]$ so that, if in the equation (II) we replace $F_s(u)$ by $g_{2k}(u)$,

$$(-1)^{k-1} \frac{B_k}{2k!} z^{2k} = x^{2k-1} \sum_{\mu=0}^{\mu=[x]} g_{2k}\left(\frac{\mu y}{x}\right), \quad \dots \quad (\text{III})$$

the thus defined function z is algebraically expressed in x and y . But as well as in the equations (I) and (II) z is still discontinuous for integer values of x in equation (III). By a slight alteration it is possible to make these discontinuities disappear. Without altering the value of z for integer values of x and y we may write instead of (III)

$$(-1)^{k-1} \frac{B_k}{2k!} z^{2k} = x^{2k-1} \left\{ \sum_{\mu=1}^{\mu=[x]} g_{2k}\left(\frac{\mu y}{x}\right) + \frac{1}{2} g_{2k}(0) + g_{2k}(y) P(x) \right\} \dots (\text{IV})$$

and the function z has become continuous everywhere. The same however is not true for the partial derivatives of z with respect to x or y ; besides there is as in equations (I) and (II) a lack of symmetry. By interchanging x and y the value of z alters. To some extent these disadvantages may be eliminated. The process of integration is apt to level finite discontinuities, moreover symmetry may be introduced by it. And indeed a suitable expression of z in the form of a definite integral can be given.

We consider the function z defined by

$$\frac{B_k}{2k!} z^{2k} = x^k y^k \int_0^1 g_k(xu) g_k(yu) du \quad \dots \quad (\text{V})$$

Now z depends symmetrically on x and y and is continuous throughout. The function has continuous derivatives; we may differentiate z a number of $k-1$ times with respect to x and also $k-1$ times with respect to y , either separately or subsequently, before the derivatives lose their continuity, so that by making k larger and larger the behaviour of z tends more and more to that of an analytical function of two real variables.

We now again substitute in (V) $x = \alpha D$, $y = \beta D$ and as the trigonometrical series $g_k(xu)$ and $g_k(yu)$ are absolutely convergent (under the supposition $k > 1$) we may multiply termwise and integrate the partial products.

But after integration a nonvanishing amount is furnished only by those partial products

$$\frac{\sin}{\cos} 2\pi h \alpha D u \quad \frac{\sin}{\cos} 2\pi l \beta D u,$$

in which we have

$$h = g\beta, \quad l = g\alpha;$$

hence we find

$$\frac{B_k}{2k!} z^{2k} = \frac{4D^{2k}}{(2\pi)^{2k}} \cdot \frac{1}{2} \sum_{y=1}^{y=\infty} \frac{1}{y^{2k}} = \frac{B_k}{2k!} D^{2k}$$

and as before

$$z = D.$$

Had we integrated the product $g_m(xu) g_n(yu)$, where $m + n$ is even, instead of $g_m(xu) g_m(yu)$ the result would have been similar, only symmetry would have been lost.

We may remark that the z in equation (V) is still an algebraical function. For remembering that

$$\frac{d}{du} g_k(u) = g_{k-1}(u),$$

$$g_1(u) = P(u),$$

we deduce by repeated partial integration

$$\begin{aligned} \frac{B_k}{2k!} z^{2k} &= \sum_{\nu=0}^{\nu=k-2} (-1)^\nu x^{k+\nu} y^{k-1-\nu} g_{k-\nu}(x) g_{k+\nu+1}(y) + \\ &+ (-1)^{k-1} x^{2k-1} \{g_1(xu) g_{2k}(yu)\}_{u=0}^{u=1} + (-1)^k \frac{x^{2k}}{y} g_{2k+1}(y), \end{aligned}$$

or finally

$$\begin{aligned} \frac{B_k}{2k!} z^{2k} &= \sum_{\nu=0}^{\nu=k-2} (-1)^\nu x^{k+\nu} y^{k-1-\nu} g_{k-\nu}(x) g_{k+\nu+1}(y) + \\ &+ (-1)^k \frac{x^{2k}}{y} g_{2k+1}(y) + \\ &+ (-1)^{k-1} x^{2k-1} \left\{ \sum_{\nu=1}^{\nu=\lceil x \rceil} g_{2k} \left(\frac{\mu y}{x} \right) + \frac{1}{2} g_{2k}(0) + g_{2k}(y) P(x) \right\}. \quad (VI) \end{aligned}$$

From this equation we infer that the product $z^{2k}xy$ is a rational integral function of x and y of degree $4k + 2$, and generally speaking the equation represents an algebraical surface S of that degree. But it should be noticed that this surface S in reality is composed of an infinite number of partial surfaces, having contact more or less close along a system of plane curves C . And in fact the larger the integer k be chosen the closer will be the contact of the partial surfaces. Equation (VI) contains the equations of all the partial surfaces, but each of them has a distinct equation the coefficients of which are made up from the integers

$$[x], [y] \text{ and } \left[\frac{\mu y}{x} \right], \quad (\mu = 1, 2, 3, \dots [x]).$$

Hence we pass from one partial surface to an adjacent one in all places, where one at least of these integers increases by unity.

Thus the projections on the xy -plane of the curves C are of two distinct categories. To the first belong the straight lines $x=n$, $y=n$, regularly dividing the xy -plane in equal squares of side unity. The second category is formed by straight lines issuing from the vertices of these squares and which, if produced, would pass through the origin. The number of these lines, which have their points of issue inside the square, bounded by the x -axis, the y -axis and by the lines $x=n$, $y=n$ is seen to be $2\Sigma q(n)^1$, that is on an average equal to $\frac{6}{\pi} n^2$. Therefore the partial surfaces remote from the origin ultimately take the form of infinitely narrow strips, the length of which varies from 1 to $\sqrt{2}$.

In order to lower as far as possible the degree of the surface S , we should take $k=1$ and we have from (V) and (VI)

$$\frac{1}{12} z^2 = xy \int_0^1 P(xu)P(yu)du = x \left\{ \sum_{\mu=1}^{x=[x]} g_2 \left(\frac{\mu y}{x} \right) + \frac{1}{2} g_2(0) + g_2(y)P(x) \right\} - \frac{x^2}{y} g_3(y).$$

A comparison with (IV) makes it evident that for integer values of x and y the quantity z still becomes equal to the greatest common divisor. The surface S is of the 6th degree, the partial surfaces still hang together everywhere but in this case they have no contact along the curves C .

Physics. — “*On maxima and minima of intensity sometimes observed within the shading of strongly widened spectral lines.*”²⁾
By Prof. W. H. JULIUS.

While examining a series of photographs of the solar spectrum, made by ROWLAND in 1888 and 1889, JEWELL discovered one plate on which the shading of H and K was broken up into a system of faint, nebulous lines, symmetrically arranged about the central absorption lines³⁾. The distances apart of the component lines of the series increased as the distance from the central line increased. On some other photographs of the solar spectrum, taken by ROWLAND and by himself, he only found feeble indications of these series; but

¹⁾ $\varphi(n)$ denotes the number of integers less than n and prime to n .

²⁾ Part of the contents of this communication has already been shortly mentioned in a foot-note which was added to the English translation of a former paper (Proc. Roy. Acad. Amst. IV, p. 601) but did not occur in the Dutch original of the same.

³⁾ L. E. JEWELL, *Astrophysical Journal*, III. p. 108, 1896, and VIII, p. 51—53, 1898.

in the shading of some of the strongest lines of iron and a few other elements a similar structure was observed, the component lines being faint, nebulous, and close together.

The plate which showed the structure of *H* and *K* most plainly, displayed an additional peculiarity, as on it the general shading of those lines was unusually weak.

In HALE's abnormal spectrum ¹⁾, which was characterized by the extreme weakness of the shaded background of many absorption lines, maxima and minima of intensity were also distinguishable under a microscope, though they did not appear so clear nor so regularly arranged as in the case described by JEWELL.

If we suppose the principal cause of the shading of the Fraunhofer lines not to be the absorption, but rather the anomalous dispersion of the waves, which in the spectrum are situated on either side the central absorption line ²⁾, we can easily account for the phenomenon, before mentioned, as well as for the fact, that in very rare cases only it shows distinctly.

Let us consider a narrow beam of light of an exactly defined wave-length, belonging to the shaded background of a Fraunhofer line. This beam has emerged from the deeper layers of the Sun with a certain divergence; we suppose it to proceed in the approximate direction of the structure lines of the corona (l. c. p. 597). Let its wave-length be somewhat greater than that of the absorption line; for this kind of light, the medium will then possess a positive refraction constant, and the separate rays of the beam will curve about the denser parts of the "tubular" structure. If we had supposed the wave-length to be a little less than that of the absorption line, the refraction constant would have been negative and the rays would have curved about the rarer parts of the coronal structure. In either case the divergence of our monochromatic beam will alternately diminish and increase, and this particular kind of light will reach the Earth with an intensity, determined by the degree of divergence (convergence perhaps) with which the beam left the ultimate traces of the corona.

With respect to a beam of other light, the wave-length of which differs only slightly less from that of the absorption line, the medium will have a considerably greater refraction constant, so that the rays of this particular beam may have made a bend, or part of a bend, more than those, belonging to the former beam, on their way through

¹⁾ G. E. HALE, *Astrophysical Journal*, XVI, p. 232, 1902.

²⁾ W. H. JULIUS, *Proc. Roy. Acad. Amst.* IV, p. 589—602.

the corona. This beam may, accordingly, arrive with a quite different, say a greater, divergence and consequently display a smaller intensity in the spectrum, than the neighbouring beam, first considered.

Approaching still nearer to the absorption-line we shall come across waves that reach the Earth in beams whose divergence is smaller again, showing increased intensity, etc. It is plain that in this way periodical alternations of light and dark on either side the central absorption line must arise. The waves, corresponding to the middle of one of these fringes, will have achieved exactly one whole bend (i.e. the distance between two consecutive points of inflexion of the path) more, or less, than those corresponding to the middle of the adjacent fringes.

From the familiar type of the dispersion curve it follows directly, that, in moving away from the absorption line, to equal differences in refraction constant increasing differences in wavelength will answer. The distance between the fringes will accordingly increase from the centre to either side, as has in fact been observed.

Our explanation requires besides, that this system of faint lines should be visible only when sunlight reaches us exactly along a coronal streamer of sufficient length. In my last paper (l.c.) I showed that, in case this condition is fulfilled, the average shading of the Fraunhofer lines must be abnormally weak. It is therefore not to be wondered at, that on the plate, plainly displaying the peculiar structure of *H* and *K*, the shading really was unusually faint. But the formation of a well defined line-system demands a further condition to be fulfilled, viz. that the configuration of that part of the (rotating) corona we are just looking through, offers all but the same aspect as long as the photographic plate is exposed. This, of course, requiring very special circumstances, we see why even in cases, in which the shading of the Fraunhofer lines is weak, the fringes may be missing all the same.

In a few cases has a like structure been observed with some strongly widened emission lines of the arc-spectrum. KAYSER came across this phenomenon in a line of the lead-spectrum ¹⁾; ROWLAND too seems to have observed it once; and after many vain endeavours JEWELL succeeded in obtaining a photograph of the arc spectrum of calcium, in which at *H* and *K* the series appeared rather distinctly. This plate was obtained by using an extremely powerful direct current and exposing for three or four seconds only. Under these conditions

¹⁾ H. KAYSER, Handbuch der Spectroscopie, II, p. 353.

the heated calcium vapour formed a much more extended atmosphere around the poles than with a weaker current.

KAYSER¹⁾ asserts, though, that it has hitherto remained unknown, what are the exact conditions upon which the phenomenon depends.

In connection with the preceding considerations, I hold it possible that in those experiments the metallic vapour has, during the (short) exposures, formed a kind of flame of tubular structure, which happened to be in the exact direction of the spectroscope. This view seems reasonable if we bear in mind the well-known "blowing" which is of frequent occurrence in a powerful arc loaded with much vapour. The radiations, proceeding from the core of the arc, which caused the wide emission band, underwent anomalous dispersion in the enveloping vapour and traversed the flame-shaped streamer, following sinuous paths.

A simple experiment convinced me that the peculiar light-distribution observed in all strongly widened Fraunhofer lines²⁾, may be strikingly imitated in the absorption-spectrum of sodium vapour. The only thing necessary was to force the absorbing vapour into a more or less tubular structure, such as we presumed it to exist in the corona.

A slightly converging beam of electric light was thrown on to the slit of a grating-spectrocope. At a distance of rather more than 100 c.m. from the slit, and about 1,5 c.m. below the axis of the beam was the opening of a specially constructed bunsen-burner, from which a sodium-flame emerged. This opening was slit-shaped (30 c.m. long, 0,2 c.m. wide) and adjusted in a position exactly parallel with the axis of the incident beam. The pressure of the gas was somewhat variable, and a good regulator unfortunately not at hand. In order to supply the long flame with sodium, the construction of the burner included a kind of narrow gutter on either side, into which had been poured a solution of a sodium-salt. This ascended into the flame by strips of asbestos paper. When viewing this flame lengthwise, it was as if one were looking through a compressed tube, the sides of which consisted of sodium-vapour. The density of the vapour diminished gradually towards the centre as well as towards the outside.

The sodium-lines were observed in the spectrum of the third order. In spite of the great length of the flame the real absorption lines were narrow; they stood out from a pretty dark softly shaded background, the width of which amounted to several ÅNGSTRÖM units. The distribution of the light entirely corresponded to JEWELL'S

¹⁾ l. c. p. 354.

²⁾ JEWELL, *Astroph. Journ.* III, p. 101; HALE, *Astroph. Journ.* III, p. 156—161.

description of the strongly shaded Fraunhofer lines. Close to the central absorption line there was also an unmistakable increase of luminosity (resembling the supposed emission lines in the solar spectrum); but this increase ought, without doubt, to be attributed to the most strongly curved rays being kept together by the tubular structure of the flame, and not to direct radiation from the flame. For, the electric light being intercepted, the emission-lines were scarcely visible in the dark field. And besides, as soon as the flame was disturbed by blowing upon it, or when it was partially covered by a diaphragm, the bright band, as well as the shading, became unsymmetrical with respect to the absorption line. Neither DOPPLER'S principle, nor the influence of pressure on wave-length can here have played an appreciable part.

I moreover observed fringe-like maxima and minima in the shadings, but they showed irregular and so unsteady, that I could not think of measuring their distances. Nor can there be any question of photographing this peculiarity before means have been devised to keep a structure of sodium vapour, as described above, steady for a reasonable time. Such means are however being prepared.

Imperfect as our present experiment must be, it still serves to bear out the assertion, that numerous peculiarities of the solar spectrum may be explained from anomalous dispersion.

Physics. — *“On the emission and absorption by metals of rays of heat of great wave-lengths.”* By H. A. LORENTZ.

§ 1. HAGEN and RUBENS have recently shown by their measurements of the reflecting power of metals ¹⁾ that the behaviour of these bodies towards rays of great wave-lengths (larger than $8\ \mu$) may be accounted for, if one applies to the propagation of electric vibrations the equations that hold for slowly varying currents, and which contain no other physical constant of the metal but its conductivity. It follows from this result that a theory which can give an adequate idea of the mechanism of a current of conduction will also suffice for the explanation of the absorption of the rays that have been used by these experimenters. A theory of this kind has been developed by RIECKE ²⁾ and DRUDE ³⁾. According to their views a metal contains an immense number of free electrons moving to and fro in much the same way as the molecules of a gas or as the ions in an electrolytic solution,

¹⁾ HAGEN and RUBENS, Berliner Sitzungsberichte, 1903, p. 269; Berichte d. deutschen phys. Gesellsch., 1903, p. 145.

²⁾ RIECKE, Wied. Ann., Bd. 66, p. 353, 1898.

³⁾ DRUDE, Drude's Ann., Bd. 1, p. 566, 1900.

the velocity of agitation increasing with the temperature. It is to be assumed that, in this "heat-motion", every electron travels along a straight line, until it strikes against a particle of the metal; the path will therefore be an irregular zigzag-line and, so long as there is no cause driving the electrons in a definite direction, an element of surface will be traversed by equal numbers of electrons, travelling to opposite sides. Things will be different if the metal is exposed to an electric force. The motion of the electrons will still be an irregular agitation; yet, motions in a definite direction will predominate, and this will show itself in our observations as an "electric current."

Now we may infer from the relation between absorption and emission that is required by KIRCHHOFF'S law, that the mechanism by which the emission of a body is produced is the same as that to which it owes its absorbing power. It is therefore natural to expect that, if we confine ourselves to the case of great wave-lengths, we shall be able to explain the emission of a metal by means of the heat-motion of its free electrons, without recurring to the hypothesis of "vibrators" of some kind, producing waves of definite periods.

In the following pages this idea has been worked out. After having calculated the emissive power we shall find that its ratio to the absorbing power does not depend on the value of those quantities by which one metal differs from another. According to the law of KIRCHHOFF, the result may be considered as representing the ratio between the emission and the absorption for an arbitrarily chosen body, or as the emissive power of a perfectly black substance; it will be found to contain a certain constant quantity, whose physical meaning will appear from the theory.

§ 2. The ratio of which I have just spoken is intimately connected with another important physical quantity, viz. the density of the energy of radiation in a space enclosed by perfectly black walls, which are kept at a uniform absolute temperature T . If the electromagnetic motions of which the aether in such a space is the seat, are decomposed into rays travelling in all directions, and each of which has a definite wave-length, the energy per unit volume, in so far as it belongs to rays with wave-lengths between λ and $\lambda + d\lambda$, may be represented by

$$F(\lambda, T) d\lambda,$$

F being a function which many physicists have tried to determine. BOLTZMANN and WIEN have shown by thermodynamical reasoning that the above expression may be written

$$\frac{1}{\lambda^5} f(\lambda T) d\lambda, \dots \dots \dots (1)$$

where $f(\lambda T)$ is a function of the product λT . Afterwards PLANCK ¹⁾ has found for (1) the form

$$\frac{8 \pi c h}{\lambda^5} \cdot \frac{1}{e^{\frac{ch}{k\lambda T}} - 1} d\lambda, \dots \dots \dots (2)$$

Here c is the velocity of light in aether and h and k are universal constants.

In the theory of PLANCK every ponderable body is supposed to contain a great many electromagnetic vibrators, or, as PLANCK calls them, "resonators", each of which has its own period of free vibration, and which exchange energy with the aether as well as with the molecules or atoms of ponderable matter. The conditions of statistical equilibrium between the resonators and the aether may be thoroughly investigated by means of the equations of the electromagnetic field. As to the partition of energy between the vibrations of the resonators and the molecular motions in the body, PLANCK has not endeavoured to give an idea of the processes by which it takes place. He has used other modes of reasoning, of which I shall only mention one, which is to be found in his later papers on the subject and which consists in the determination of that distribution of energy that is to be considered as the most probable. I shall not here discuss the way in which the notion of probability is introduced in PLANCK's theory and which is not the only one that may be chosen. It will suffice to mention an assumption that is made about the quantities of energy that may be gained or lost by the resonators. These quantities are supposed to be made up of a certain number of *finite* portions, whose amount is fixed for every resonator; according to PLANCK, the energy that is stored up in a resonator cannot increase or diminish by gradual changes, but only by whole "units of energy", as we may call the portions we have just spoken of. Besides, PLANCK has found it necessary to ascribe to these units a magnitude depending on the frequency n of the free vibrations of the resonator, the magnitude being represented by $\frac{hn}{2\pi}$.

As to the constant k , it has a very simple physical meaning; $\frac{3}{2} kT$ is the mean kinetic energy of the molecule of a gas at the temperature T .

¹⁾ PLANCK, Drude's Ann., Bd. 1, p. 69, 1900; Bd. 4, p.p. 553 and 564, 1901.

It appears from the above remarks that the hypothesis regarding the finite "units of energy", which has led to the introduction of the constant h , is an essential part of the theory; also that the question as to the mechanism by which the heat of a body produces electromagnetic vibrations in the aether is still left open. Nevertheless, the results of PLANCK are most remarkable. His formula represents very exactly the energy of the radiations for all values of the wave-lengths, whereas the following considerations are from the outset confined to long waves. We may at best expect to deduce from them the form which the function in (1) takes for this extreme case.

§ 3. Since, if we trust to KIRCHHOFF's law, the ratio between the emission and the absorption must be regarded as independent of the dimensions and the position of the body considered, we may simplify the problem by an appropriate choice of circumstances. I shall therefore consider a plate with parallel plane surfaces and I shall suppose its thickness Δ to be so small that the absorption may be reckoned proportional to it and that the energy emitted by the posterior layers may be supposed to pass through the plate without any sensible absorption. I shall also confine myself to the absorption of perpendicularly incident rays and to the emission in directions making infinitely small angles with the normal.

Let σ be the conductivity of the metal, i. e. the constant ratio between the electric current and the electric force, these latter quantities being expressed in the modified electrostatic units I have lately introduced.¹⁾ Then the absorbing power of the plate, the coefficient by which we must multiply the energy of normal incident rays, in order to get the absorbed energy, is given by²⁾

$$A = \frac{\sigma}{c} \Delta \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Here we shall substitute for σ the value furnished by DRUDE's theory. Let the metal contain different kinds of free electrons, which we may distinguish as the 1st, the 2nd, the 3rd kind, etc., and let us suppose that all electrons of one and the same kind have equal charges, equal velocities of heat-motion, or, as we may say, "molecular" velocities, and travel over paths of equal mean length between two successive encounters with particles of the metal.

We shall write e_1, e_2, \dots for the charges of the different kinds of electrons, u_1, u_2, \dots for the mean molecular velocities, l_1, l_2, \dots

¹⁾ LORENTZ, Proceedings Acad. of Science, Amsterdam, Vol. 11, p. 608, 1903.

²⁾ See § 12 below. In electromagnetic units the formula becomes

$$A = 4\pi c \sigma \Delta.$$

for the mean lengths of the free paths, N_1, N_2, \dots for the number of electrons of the several kinds, contained in unit of volume. We shall finally suppose, as DRUDE has done, that for every kind of electrons, the mean kinetic energy of one of these particles is equal to that of a molecule of a gas at the same temperature; we may represent it by αT , if T is the absolute temperature, and α a constant.

In these notations DRUDE's value is ¹⁾

$$\sigma = \frac{1}{4\alpha T} (e_1^2 N_1 l_1 u_1 + e_2^2 N_2 l_2 u_2 + \dots), \quad . \quad . \quad . \quad (4)$$

so that (3) becomes

$$A = \frac{1}{4\alpha c T} (e_1^2 N_1 l_1 u_1 + e_2^2 N_2 l_2 u_2 + \dots) \Delta. \quad . \quad . \quad (5)$$

It is to be remarked that the formula (4) has been obtained in the supposition that the electric force remains constant, or at least that it keeps its direction and magnitude during an interval of time in which an electron has undergone a large number of collisions against particles of the metal. The results of HAGEN and RUBENS are therefore favorable to the view that even the period of vibration of the rays is very large in comparison with the time between two succeeding impacts. Part of the following calculations are based on this assumption.

§ 4. We have now to examine the emission by the plate. It follows from the fundamental equations of the theory of electrons, that every *change*, whether in direction or in magnitude, of the velocity of an electron produces an electromagnetic disturbance travelling outwards in the surrounding aether. Hence, it will be at the instants of the collisions that the electrons become centres of radiation. We shall calculate the amount of energy, radiated in this way, in so far as it is emitted across a definite part ω of the front surface of the plate; this part of the emission is due to the electrons contained in a volume $\omega\Delta$ of the metal.

Let O be a point within the area ω , OP the normal in this point, drawn towards the side of the aether, and P a point on this line, at a distance r from O , which is very large in comparison with the dimensions of ω . In this point P we place an element of surface ω' , perpendicular to OP ; our problem will be to calculate the energy radiated across this element. I choose O as origin of coordinates and OP as the axis of z . The components of the velocity of an electron will be denoted by u_x, u_y, u_z .

¹⁾ DRUDE, l. c., p. 576. This formula does not change by the introduction of our new units.

Now, if an electron with charge e , is in O at the time t , and has at that instant the accelerations $\frac{du_x}{dt}$, $\frac{du_y}{dt}$, $\frac{du_z}{dt}$, it will produce at the point P , at the time $t + \frac{r}{c}$, a dielectric displacement, whose components are ¹⁾

$$-\frac{e}{4\pi c^2 r} \frac{du_x}{dt}, \quad -\frac{e}{4\pi c^2 r} \frac{du_y}{dt}, \quad 0 \quad . \quad . \quad . \quad . \quad . \quad (6)$$

On account of the great length of OP , these expressions may also be applied to an electron situated, not in O but in any other point of the part of the plate corresponding to the area ω . The whole dielectric displacement in P in the direction of x (it is only this component that will be considered in the next paragraphs) at the time $t + \frac{r}{c}$ will therefore be

$$d_x = -\frac{1}{4\pi c^2 r} \sum e \frac{du_x}{dt}, \quad . \quad . \quad . \quad . \quad . \quad (7)$$

if the sum is extended to all electrons present in the volume $\omega \Delta$ at the time t .

There will also be a magnetic force of the same numerical value, and by POYNTING's theorem a flow of energy across the element ω' , in the direction from the plate towards P . The amount of this flow per unit of time is given by

$$c d_x^2 \cdot \omega' \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

§ 5. It will be necessary for our purpose to decompose the whole emission into rays of different wave-lengths and to examine the part of (8) corresponding to the rays that have their wave-lengths within certain limits. This may be done by means of FOURIER's series.

Let us consider a *very long* time, extending from $t=0$ to $t=\vartheta$. During this interval the value of d_x at the point P will continually change in a very irregular way; it may however in every case be expanded in the series

$$d_x = \sum_{m=1}^{m=\infty} a_m \sin \frac{m\pi t}{\vartheta}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

whose coefficients are given by

$$a_m = \frac{2}{\vartheta} \int_0^{\vartheta} \sin \frac{m\pi t}{\vartheta} d_x dt. \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

¹⁾ The proof of this will be found in one of the next parts of my "Contributions to the theory of electrons."

Now, if the plate is kept at a constant temperature, the radiation will also be stationary and \mathfrak{d}_x^2 may be replaced by its mean value

$$\overline{\mathfrak{d}_x^2} = \frac{1}{\mathfrak{D}} \int_0^{\mathfrak{D}} \mathfrak{d}_x^2 dt$$

during the time \mathfrak{D} . Substituting the value (9), we get integrals of two different kinds, some containing the square of a sine, and others the product of two sines. The integrals of the second kind will disappear, and

$$\int_0^{\mathfrak{D}} \sin^2 \frac{m\pi t}{\mathfrak{D}} dt = \frac{1}{2} \mathfrak{D},$$

so that

$$\overline{\mathfrak{d}_x^2} = \frac{1}{2} \sum_{m=1}^{m=\infty} a_m^2. \quad (11)$$

As to the frequency of the terms in (9), it is given by

$$n = \frac{m\pi}{\mathfrak{D}}; \quad (12)$$

it will therefore increase by equal differences $\frac{\pi}{\mathfrak{D}}$, if we give to m its successive values.

By choosing for \mathfrak{D} a value sufficiently large, we may make this step $\frac{\pi}{\mathfrak{D}}$ as small as we like, so that ultimately, even between two values of the frequency n and $n + dn$, which are in a physical sense infinitely near each other, there will be a certain number of values of (12) and of corresponding terms in the series (11). The number of these terms will be $\frac{\mathfrak{D}}{\pi} dn$, hence, if we suppose a_m , or

$$a_m = \frac{2}{\mathfrak{D}} \int_0^{\mathfrak{D}} \sin nt \cdot \mathfrak{d}_x dt, \quad (13)$$

to have the same value for each term of this group, the corresponding part of (11) will be

$$\frac{\mathfrak{D}}{2\pi} a_m^2 dn.$$

Substituting this for \mathfrak{d}_x^2 in (8), we get for the radiation across ω' , due to the rays with frequencies between n and $n + dn$,

$$\frac{c\mathfrak{D}}{2\pi} \omega' a_m^2 dn. \quad (14)$$

§ 6. We have now to calculate the coefficient a_m by means of (13). After having substituted in the integral the value (7), we may still take for its limits 0 and \mathfrak{A} , provided we reckon the time from an instant, preceding by the interval $\frac{r}{c}$ the moment from which it has been reckoned till now. Thus:

$$a_m = -\frac{1}{2\pi c^2 \mathfrak{A} r} \sum \left[e \int_0^{\mathfrak{A}} \sin nt \cdot \frac{du_x}{dt} dt \right],$$

or, after integration by parts, since $\sin nt$ vanishes at the limits,

$$a_m = \frac{n}{2\pi c^2 \mathfrak{A} r} \sum \left[e \int_0^{\mathfrak{A}} \cos nt \cdot u_x dt \right]. \quad . \quad . \quad . \quad . \quad (15)$$

The sum in these expressions relates to all the electrons in the part $\omega\Delta$ of the plate and it is by reason of the immense number of these particles that a definite value may be assigned to a_m^2 .

We shall begin by determining a_m^2 and the amount of the radiation in the supposition that there are only free electrons of one kind (§ 3). We shall write $\eta = N\omega\Delta$ for their number, e for the charge of each of them, and we shall further simplify the problem by supposing that the molecular velocity u , the same for all the electrons, is not altered by the collisions and that all the paths between two successive impacts have exactly the same length l . Then, the time

$$\tau = \frac{l}{u}$$

will also have a definite length.

§ 7. Let t_1, t_2, t_3, \dots be a series of instants, between 0 and \mathfrak{A} , at intervals τ from each other. Then it is clear that, if we fix our attention on the positions of a single electron at these instants, we shall have one point on each of the sides of the zigzag-line described by this particle.

Now we may in the first place determine the integral in (15) for the lapse of time during which an electron travels over the side of the zigzag-line on which it is found at the time t_k . As the length τ of this interval is much shorter than the period $\frac{2\pi}{n}$ of the factor $\cos nt$, we may write for the integral

$$\cos nt_k \cdot \tau u_x. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

It is clear that we shall obtain the sum in (15), for the η electrons,

if, after having multiplied (16) by e , we perform the two summations, indicated in the formula

$$a_m = \frac{n e \tau}{2 \pi c^2 \vartheta r} \sum_k [\cos n t_k \sum u_x]. \quad (17)$$

We have in the first place to take the sum of all the values of u_x for the system of electrons, at a particular instant t_k , and then to add together all the results obtained in this way for the instants t_1, t_2 , etc.

§ 8. If we wish to find $\sum u_x$ for a given time, we must keep in mind that the velocities u of the electrons have at that instant very different directions. We may represent all these velocities by vectors drawn from a fixed point C . The ends D of all these vectors will lie on a sphere with radius u , and if we let fall from each of these points a perpendicular DD' on the diameter of this sphere that is parallel to OX , the distances of the projections from C will give the values of u_x . The sum of all these values may therefore be represented by

$$\sum u_x = q \xi,$$

if ξ is the positive or negative distance at which the centre of gravity of the points D' , considered as equal to each other, is situated from the centre C .

Of course, on account of the large number of the points, this distance will be very much smaller than the radius u , and, if we repeat the construction of the diagram of velocities for each of the instants $t_1, t_2 \dots$, the small value that is found for ξ will be positive in one case and negative in another. It is to be remarked in this respect that there is no connexion at all between the values of ξ , which we shall find for two succeeding instants in the series $t_1, t_2 \dots$. Indeed, between any two such instants, every electron will have undergone a collision, and it may safely be assumed that, whatever be the direction of motion of an electron before the impact, all directions will be equally probable after the impact¹⁾.

Now, in order to determine a_m^2 , we have to take the square of the sum denoted by \sum_k in the formula (17). This square consists of terms of two kinds, some having the form

$$\cos^2 n t_k [\sum u_x]_{t_k}^2 = q^2 \cos^2 n t_k \xi_k^2 \quad (18)$$

1) This is easily shown, as has been done by MAXWELL in his first paper on the kinetic theory of gases, if both the electrons and the particles of the metal are supposed to be perfectly elastic spheres.

and others the form

$$2 \cos n t_k \cos n t_{k'} [\Sigma u]_{t_k} [\Sigma u]_{t_{k'}} = 2 q^2 \cos n t_k \cos n t_{k'} \xi_k \xi_{k'} \dots \quad (19)$$

As has already been said, the time ϑ contains a very large number of periods $\frac{2\pi}{n}$. A certain value of $\cos nt$, once occurring in the series $\cos nt_1, \cos nt_2, \cos nt_3, \dots$ may therefore be supposed to repeat itself many times. Also, one and the same value of the product $\cos nt_k \cos nt_{k'}$ may be said to occur for many different values of k and k' . Such a product will therefore have to be multiplied by very different expressions of the form $\xi_k \xi_{k'}$, and, since the different values of ξ are mutually independent, the number of cases in which ξ_k and $\xi_{k'}$ have opposite signs will be equal to that in which they have the same sign. It appears in this way that the terms (19) will cancel each other in the sum. It is only the terms of the form (18) that remain, and we shall have

$$a_m^2 = \frac{n^2 e^2 \tau^2 q^2}{4 \pi^2 c^4 \vartheta^2 r^2} \sum_k [\cos^2 n t_k \cdot \xi_k^2] \dots \dots \dots \quad (20)$$

§ 9. Here we may begin by taking together those terms in which $\cos nt_k$ has one and the same value. Let the number of these be Q . Then, we have to repeat Q times the construction of the diagram of velocities, and it may be asked in how many of these Q cases ξ will lie between given limits ξ and $\xi + d\xi$, or, what amounts to the same thing, what is the probability for ξ falling between these limits.

This question may be reduced to a simpler problem. A series of planes, perpendicular to OX and at equal distances from one another, will divide the spherical surface into equal parts. Therefore, instead of distributing the points D on the surface in an irregular, arbitrarily chosen manner, we may as well immediately distribute the points D' at random over the diameter, without giving any preference to one part of the line over another. The probability in question is thus found to be ¹⁾

$$Pd\xi = \frac{1}{u} \sqrt{\frac{3q}{2\pi}} e^{-\frac{3q}{2u^2} \xi^2} d\xi \dots \dots \dots \quad (21)$$

Hence, among the Q terms in the sum, occurring in (20), for which the factor $\cos^2 nt_k$ has equal values, there will be $Q Pd\xi$ terms, which may be said to have the same ξ_k . Together, they will contribute to the sum the amount

¹⁾ See §§ 13—15.

different kinds of electrons. The final result is therefore ¹⁾

$$\frac{n^2}{24\pi^3 c^3 r^2} (e_1^2 N_1 l_1 u_1 + e_2^2 N_2 l_2 u_2 + \dots) \Delta \omega \omega' dn. \quad (24)$$

§ 10. If now we divide (24) by (5), all quantities N, e, u and l , by which one metal differs from another, disappear. This is what might be expected according to KIRCHHOFF's law and the result

$$\frac{an^2 T}{6\pi^3 c^2 r^2} \omega \omega' dn$$

may be taken to express the emission by a perfectly black body under the circumstances we have supposed. It represents the amount of energy which, in the case of such a body, is transmitted per unit of time across an element ω' , in the rays whose frequency lies between n and $n + dn$ and whose directions deviate infinitely little from the normal to the element, being contained within a solid angle $\frac{\omega}{r^2}$. Multiplying by $\frac{4\pi r^2}{c\omega\omega'}$, we are led to the following expression for the density of energy of which I have spoken in § 2 :

$$\frac{2an^2 T}{3\pi^2 c^3} dn. \quad (25)$$

Taking for the group of rays those whose wave-lengths are included between λ and $\lambda + d\lambda$, we get for the corresponding energy per unit volume

$$\frac{16}{3} \frac{\pi a T'}{\lambda^4} d\lambda. \quad (26)$$

¹⁾ It is easy to free ourselves from the hypothesis that for all electrons of one kind there is a single length of path l and a single molecular velocity u . Indeed, the motion of an electron along one of the small straight lines l , which it describes between the instants 0 and \mathfrak{S} , will furnish for the sum in (15) a quantity

$$e \cos nt \cdot u_x \tau,$$

if u is the velocity for the particular line l we wish to consider, and τ the time required for the motion along it.

Now, among all these rectilinear motions between two successive encounters, of one kind of electrons, we may select those for which u and l have certain definite values and we may begin by calculating the coefficient a_m and the emission, in so far as they depend on the part of (15) which corresponds to these particular motions; in doing so, we may use the method shown in §§ 7—9. The total emission may be regarded as the sum of all the partial values (with different l 's and different u 's) thus obtained, and after all the expression (24) will still hold, provided we understand by $l_1, l_2 \dots$ certain mean lengths of path and by $u_1, u_2 \dots$ certain mean molecular velocities. We need not however enter into these details, because the conductivity and the coefficient of absorption have not been calculated with a corresponding degree of accuracy.

This is found from (25) by using the relation $n = \frac{2\pi c}{\lambda}$.

§ 11. The result of the preceding calculations not only conforms to the law of KIRCHHOFF; it has also a form agreeing with those of BOLTZMANN and WIEN. Indeed, the expression (26) follows from (1), if we put

$$f(\lambda T) = \frac{16}{3} \pi \alpha \cdot \lambda T.$$

Our last task will be to evaluate the constant α by applying the formula (26) to experimental determinations of the radiation of black bodies, and to compare the result with what has been inferred about the same constant from other classes of phenomena. Combining the measurements of LUMMER and PRINGSHEIM¹⁾, who have gone far into the infra-red, with the absolute amount of the radiation as determined by KURLBAUM²⁾, I find

$$\alpha = 1,6 \cdot 10^{-16} \frac{\text{erg}}{\text{degree}}.$$

On the other hand, we get, starting from VAN DER WAALS' evaluation of the mass of an atom of hydrogen,

$$\alpha = 1,2 \cdot 10^{-16}.$$

A comparison of my formula with that of PLANCK is also interesting. For very large values of the product λT , the denominator in (2) becomes $\frac{ch}{k\lambda T}$, and the expression itself $\frac{8\pi kT}{\lambda^4} d\lambda$. This agrees with (26), if $\alpha = \frac{3}{2} k$.

Now the mean kinetic energy of a molecule of a gas would be $\frac{3}{2} kT$ according to PLANCK and has been represented in what precedes by αT . There appears therefore to be a full agreement between the two theories in the case of long waves, certainly a remarkable conclusion, as the fundamental assumptions are widely different.

On the absorption by a thin metallic plate.

§ 12. Take the origin of coordinates in the front surface, the axis of z towards the metal, and let there be free aether on both sides.

Writing \mathfrak{E} for the electric force, \mathfrak{J} for the current of conduction,

¹⁾ LUMMER and PRINGSHEIM, Verhandl. d. deutschen phys. Gesellsch., 1900, p. 163.

²⁾ KURLBAUM, Wied. Ann., Bd. 65, p. 754, 1898.

\mathfrak{H} for the magnetic force and putting the magnetic permeability = 1, we have for the metal

$$\text{rot } \mathfrak{H} = \frac{1}{c} \mathfrak{J}, \quad \text{rot } \mathfrak{E} = -\frac{1}{c} \dot{\mathfrak{H}}, \quad \mathfrak{J} = \sigma \mathfrak{E}.$$

It is found by these equations that in electromagnetic waves travelling in the direction of the positive z , \mathfrak{E} and \mathfrak{H} can have the directions of OX and OY , and values equal to the real parts of the complex quantities

$$\mathfrak{E}_x = a e^{int - \alpha(1+i)z}, \quad \mathfrak{H}_y = \kappa a e^{int - \alpha(1+i)z} \quad . \quad . \quad (27)$$

a being the amplitude of the electric force, and the constants α and κ being given by

$$\alpha = \frac{1}{c} \sqrt{\frac{1}{2} n \sigma}, \quad \kappa = (1-i) \sqrt{\frac{\sigma}{2n}}.$$

Similarly, waves travelling in the opposite direction may be represented by

$$\mathfrak{E}_x = a e^{int + \alpha(1+i)z}, \quad \mathfrak{H}_y = -\kappa a e^{int + \alpha(1+i)z} \quad . \quad . \quad (28)$$

For the aether the corresponding formulae are somewhat simpler; in the first case

$$\mathfrak{E}_x = a e^{int - i \frac{n}{c} z}, \quad \mathfrak{H}_y = a e^{int - i \frac{n}{c} z} \quad . \quad . \quad . \quad (29)$$

and in the second

$$\mathfrak{E}_x = a e^{int + i \frac{n}{c} z}, \quad \mathfrak{H}_y = -a e^{int + i \frac{n}{c} z} \quad . \quad . \quad . \quad (30)$$

Now, if rays fall perpendicularly on the front surface of the plate, we may unite all the systems of waves arising from the repeated reflexions into the following parts: 1st. a reflected system in the aether, 2nd. transmitted waves in the aether behind the plate, 3rd. waves in the plate, travelling towards the back surface and 4th. rays in the metal, going in the opposite direction. Representing the incident rays and the motions mentioned under these four heads by the equations (29), (30), (29), (27), (28), with the values a_1, a_2, a_3, a_4, a_5 of the amplitude, we have, in virtue of the conditions at the two surfaces (continuity of \mathfrak{E}_x and \mathfrak{H}_y)

$$\begin{aligned} a_1 + a_2 &= a_4 + a_5, \\ a_1 - a_2 &= \kappa(a_4 - a_5), \\ a_4 e^{-s} + a_5 e^{+s} &= a_3 e^{-i \frac{n}{c} \Delta}, \\ \kappa a_4 e^{-s} - \kappa a_5 e^{+s} &= a_3 e^{-i \frac{n}{c} \Delta}, \end{aligned}$$

In these formulae, Δ is the thickness of the plate, and

$$\alpha(1+i)\Delta = s \quad . \quad . \quad . \quad . \quad . \quad . \quad (31)$$

The solution; in so far as it is necessary to our purpose, is

$$a_2 = \frac{(\kappa^2 - 1)(e^{-s} - e^{+s})}{(\kappa + 1)^2 e^{+s} - (\kappa - 1)^2 e^{-s}} a_1,$$

$$a_3 = \frac{4\kappa}{(\kappa + 1)^2 e^{+s} - (\kappa - 1)^2 e^{-s}} e^{i\frac{n}{c}\Delta} a_1.$$

In these expressions Δ and consequently s are now to be supposed infinitely small. Replacing e^{-s} and e^{+s} by $1-s$ and $1+s$, one finds

$$a_2 = -\frac{1}{2}\left(\kappa - \frac{1}{\kappa}\right)s a_1,$$

$$a_3 = \left[1 - \frac{1}{2}\left(\kappa + \frac{1}{\kappa}\right)s\right] e^{i\frac{n}{c}\Delta} a_1$$

The first of these equations shows that the amplitude of the rays reflected by the thin plate is infinitely small, so that we may neglect their energy as a quantity of the second order.

As to the transmitted rays, the amount of energy propagated in them will be equal to the product of the incident energy by the square of the modulus of the complex expression

$$\left[1 - \frac{1}{2}\left(\kappa + \frac{1}{\kappa}\right)s\right].$$

This square is

$$1 - \frac{\sigma}{c}\Delta,$$

whence we deduce for the coefficient of absorption

$$A = \frac{\sigma}{c}\Delta.$$

On the probability with which one may expect that the centre of gravity of a large number of points distributed at random on a limited straight line will lie within given limits.

§ 13. Divide the line into a large number p of equal parts, and call these, beginning at the end A of the line, the 1st, the 2nd, the 3rd part, etc. Denote by q the number of points and let q be very much larger than p .

We shall imagine the points to be placed on the line one after another, in such a way that, whatever be the position of the points already distributed, a new point may as well fall on one part of

the line as on the other. The result will be a certain distribution of the whole number, entirely determined by chance. Let us conceive this operation to be very often repeated, say Q times, and let us calculate in how many of these Q cases, a desired distribution of the points over the p parts will occur. Dividing by Q we shall have the probability of the distribution.

The probability that there will be $a, b, \dots m$ points on the 1st, 2nd, $\dots p^{\text{th}}$ part of the line ($a + b + \dots + m = q$), is given by

$$P = \left(\frac{1}{p}\right)^q \frac{q!}{a! b! \dots m!}.$$

In the case of a very large value $\frac{q}{p}$, this probability becomes extremely small, as soon as one of the numbers $a, b, \dots m$ is far below $\frac{q}{p}$. Neglecting these small probabilities, we shall confine ourselves to those cases, in which each of the numbers $a, b, \dots m$ is very large. Then, by the well known formula of STIRLING,

$$a! = \sqrt{2a\pi} \left(\frac{a}{e}\right)^a, \text{ etc.}$$

and, if we put

$$\frac{a}{q} = a', \frac{b}{q} = b', \dots \frac{m}{q} = m',$$

we shall find

$$\log P = -\frac{1}{2}(p-1) \log(2\pi q) - q \log p - \\ - [(a'q + \frac{1}{2}) \log a' + \dots + (m'q + \frac{1}{2}) \log m'] . \quad (32)$$

It is to be remarked that the numbers $a, b, \dots m$ can only increase or diminish by whole units. The numbers $a', b' \dots m'$ can change by steps equal to $\frac{1}{q}$; this may be made so small that they may be considered as continuously variable.

§ 14. We shall in the first place determine the values of $a', b', \dots m'$ for which the probability P becomes a maximum. We have

$$d \log P = - \left[\left(q + \frac{1}{2a'} + q \log a' \right) da' + \dots + \left(q + \frac{1}{2m'} + q \log m' \right) dm' \right],$$

with the condition

$$da' + \dots + dm' = 0,$$

which is a consequence of

$$a' + \dots + m' = 1 . \quad (33)$$

The maximum will therefore be reached if

$$a' = b' = \dots = m' = \frac{1}{p},$$

so that the uniform distribution will be the most probable.

We shall next consider the probability for a distribution differing a little from the most probable one. Let us put

$$a' = \frac{1}{p} + \alpha, \quad b' = \frac{1}{p} + \beta, \quad \dots \quad m' = \frac{1}{p} + \mu. \quad (34)$$

and let us suppose the numbers $\alpha, \beta, \dots, \mu$, to be so small in comparison with $\frac{1}{p}$, that in the expansion of the quantities in (32) in ascending powers of $\alpha, \beta, \dots, \mu$, we may neglect all powers surpassing the second. We have for instance

$$\left(a'q + \frac{1}{2}\right) \log a' = -\left(\frac{q}{p} + \frac{1}{2}\right) \log p + \left(q + \frac{1}{2}p - q \log p\right) \alpha + \frac{1}{2}p \left(q - \frac{1}{2}p\right) \alpha^2,$$

where, in the last term, we may omit the term $\frac{1}{2}p$, because it is much smaller than q . If we put

$$-\frac{1}{2}(p-1) \log (2 \pi q) + \frac{1}{2}p \log p = \log P_m$$

and keep in mind that, in virtue of (33),

$$\alpha + \beta + \dots + \mu = 0, \quad . \quad . \quad . \quad . \quad . \quad (35)$$

the equation (32) becomes

$$\log P = \log P_m - \frac{1}{2}p q (\alpha^2 + \beta^2 + \dots + \mu^2),$$

$$P = P_m e^{-\frac{1}{2}p q (\alpha^2 + \beta^2 + \dots + \mu^2)}.$$

It is seen from this that P_m is the maximum of the probability, with which we shall have to do, if $\alpha = \beta = \dots = \mu = 0$. The equation shows also that, conformly to what has been said above, the probability will only be comparable to P_m so long as $\alpha, \beta, \dots, \mu$ are far below $\frac{1}{p}$. Indeed, if one of these numbers had this last value, P_m would be multiplied by

$$e^{-\frac{q}{2p}},$$

which, by our assumptions, is extremely small.

§ 15. Let $2u$ be the length of the line, x the distance along the line, reckoned from the end A , and let us take $\frac{u}{p}$ for the value or

this coordinate for all points situated on the first part of the line, $3 \frac{u}{p}$ for all points of the second part, and so on. Then, in the distribution that is characterized by $a', b', \dots m'$, the coordinate of the centre of gravity of the q points will be

$$[a' + 3 b' + 5 c' + \dots + (2 p - 1) m'] \frac{u}{p},$$

or, by (34),

$$u + [a + 3 \beta + 5 \gamma + \dots + (2 p - 1) \mu] \frac{u}{p}.$$

The positive or negative value of

$$\xi = [a + 3 \beta + 5 \gamma + \dots + (2 p - 1) \mu] \frac{u}{p} \quad . \quad . \quad (36)$$

is thus seen to represent the distance between the middle point of the line and the centre of gravity. We have to calculate the probability for this distance lying between ξ and $\xi + d\xi$.

The problem is easily solved by means of a change of variables. Instead of the quantities $a, \beta, \dots \mu$, which serve to define a mode of distribution, we shall introduce new ones $a', \beta', \dots \mu'$, the substitution being linear and orthogonal.

Let us take for the first of the new variables

$$a' = \frac{1}{\sqrt{p}} a + \frac{1}{\sqrt{p}} \beta + \dots + \frac{1}{\sqrt{p}} \mu, \quad . \quad . \quad . \quad (37)$$

and for the second

$$\beta' = -\frac{p-1}{\kappa} a - \frac{p-3}{\kappa} \beta - \dots + \frac{p-1}{\kappa} \mu, \quad . \quad . \quad . \quad (38)$$

where the numerators form an arithmetical progression, whereas κ means the positive square root of the sum of the squares of the numerators. These expressions (37) and (38) may really be adopted, because the peculiar conditions for an orthogonal substitution are satisfied: in both expressions the sum of the squares of the coefficients is 1, and we get 0 if we add together the coefficients of (37) after having multiplied them by the corresponding coefficients in (38). As to the coefficients in the expressions for $\gamma', \dots \mu'$, we may choose them as we like, provided the whole substitution remain orthogonal.

The reason for the above choice of a' and β' will be clear; the condition (35) simplifies to

$$a' = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (39)$$

and, in virtue of (35), the value (36) will be equal to

$$\xi = \frac{\kappa u}{p} \beta' \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (40)$$

in all cases with which we are concerned.

Now, the modes of distribution for which the value of ξ lies between ξ and $\xi + d\xi$ are those for which β' lies between β' and $\beta' + d\beta'$, if

$$d\beta' = \frac{p}{xu} d\xi. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (41)$$

Since $a' = 0$, every mode of distribution may be defined by the values of $\beta' \dots \mu'$, these quantities being, like $\alpha, \beta, \dots \mu$, capable of very small variations.

We can therefore select, among all the modes of distribution, those for which $\beta' \dots \mu'$ lie between β' and $\beta' + d\beta'$, γ' and $\gamma' + d\gamma'$, etc. The number of these may be represented by

$$h d\beta' \dots d\mu', \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (42)$$

where h is a coefficient whose value need not be specified. It suffices to know that it is independent of the values chosen for $\beta' \dots \mu'$. This is a consequence of the linear form of the relations between these variables and $a, b, \dots m$.

As the just mentioned modes of distribution, whose number is given by (42), differ infinitely little from one another, the probability P may be taken to be the same for each of them. Hence, the probability for the occurrence of one of these modes, no matter which, must be

$$h P d\beta' \dots d\mu' \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (43)$$

From this we may pass to the probability for β' lying between β' and $\beta' + d\beta'$, whatever be the values of $\gamma' \dots \mu'$; we have only to integrate with respect to these last variables. Now using the fundamental property of an orthogonal substitution

$$\alpha^2 + \beta^2 + \dots + \mu^2 = \alpha'^2 + \beta'^2 + \dots + \mu'^2,$$

and attending to (39), we write for (43)

$$h P_m e^{-\frac{1}{2} p q (\beta'^2 + \dots + \mu'^2)} d\beta' \dots d\mu'.$$

If we integrate this expression from $-\infty$ to $+\infty$, as may be done for obvious reasons, denoting by k a coefficient that does not depend on β' , we find for the probability in question

$$k e^{-\frac{1}{2} p q \beta'^2} d\beta'.$$

On account of (40) and (41) this is equal to

$$k' e^{-\frac{p^2 q}{2x^2 u^2} \xi^2} d\xi, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (44)$$

k' being a new constant.

It remains to introduce the value of κ^2 . According to the definition of this quantity, it is $\frac{1}{3} \rho(\rho^2 - 1)$, instead of which we may take $\frac{1}{3} \rho^3$, because ρ is a very large number. In this way (44) changes into

$$k' e^{-\frac{3q}{2a^2} \xi^2} d\xi. \quad . \quad . \quad . \quad . \quad . \quad . \quad (45)$$

We may finally determine the coefficient k' by remarking that (45), integrated from $-\infty$ to $+\infty$, must necessarily give 1. This requires that

$$k' = \frac{1}{u} \sqrt{\frac{3q}{2\pi}},$$

so that our result becomes

$$\frac{1}{u} \sqrt{\frac{3q}{2\pi}} e^{-\frac{3q}{2a^2} \xi^2} d\xi.$$

Microbiology. — “*The decomposition of cellulose by aërobic micro-organisms.*” By G. VAN ITERSSEN JR. (Communicated by Prof. M. W. BEIJERINCK).

(Communicated at the meeting March 28, 1903).

When we introduce into the soil or into natural waters substances consisting of cellulose, such as linen, cotton or paper, it will be seen, that the greater part comparatively soon disappears, whilst the cellulose derived from the continually falling dead leaves and other parts of plants is also soon destroyed under natural conditions either totally or partly. It is also a known fact that the layer of humus in the primeval forests has a limited thickness, the decrease being just compensated by the increase caused by the falling of the leaves. Investigation shows that the cellulose, although chemically so stable, is decomposed by micro-organisms. The observations by MITSCHERLICH ¹⁾, POPOFF ²⁾, VAN TIEGHEM ³⁾, TAPPEINER ⁴⁾, VAN

¹⁾ Ueber die Zusammensetzung der Wand der Pflanzenzelle, Monatsber. d. Berl. Akad., 1850, p. 102.

²⁾ Ueber Sumpfgasgährung, Archiv. f. ges. Physiol., 1875, Bd. 10, S. 113.

³⁾ Sur le bacillus amylobacter et son rôle dans la putréfaction des tissus végétaux, C. R. t. 88, 1879, p. 88. — Identité du bacillus amylobacter et du vibron butyrique de M. Pasteur, C. R. t. 89, 1879, p. 5.

⁴⁾ Ueber Celluloseverdauung, Ber. d. d. ch. G. Bd. 15, 1882, S. 999. — Ueber Cellulosegährungen, Ber. d. d. ch. G. Bd. 16, 1883, S. 1734. — Ueber die Sumpfgasgährung im Schlamm der Teiche, Sümpfe u. Kloaken, Ber. d. d. ch. G. Bd. 16, 1883, S. 1740.

SENUM¹⁾ and particularly those of HOPPE SEYLER²⁾ and of OMELIANSKI³⁾ proved, that cellulose may be broken up by anaërobic bacteria, with production of methane and carbon dioxide, or hydrogen and carbon dioxide and simultaneous formation of acetic and butyric acids. In this communication it will be shown that cellulose may also be rendered soluble by aërobic bacteria. In the first place it was proved, that this substance may serve as a source of carbon for denitrifying bacteria and may, therefore, be made to disappear with great rapidity in the presence of nitrates. But it could also be shown that cellulose is fit as a carbonfood for common aërobic bacteria and although the solution then takes place slowly, there can be no doubt about the decomposition. The products derived from the cellulose play an important role in the nutrition of other microbes particularly the spirillae, so that an elegant accumulation experiment may be based on the use of cellulose as a source of carbon.

Although the destruction of cellulose by anaërobic or aërobic bacteria requires a faintly alkaline medium, it may, with sufficient aëration, also be acted on in a faintly acid surrounding by various moulds and mycelia of higher fungi. This was first demonstrated in 1886 by DE BARY for the genus *Peziza* and the same was shown by later observers for other moulds, whilst the destruction always appeared to be due to the action of an enzyme. Here we will prove that the power possessed by moulds to attack cellulose is not confined to certain species only, as one might imagine from the existing literature, but that a great number of the species of this group share that property.

Finally, I wish to observe that I will occupy myself exclusively with the destruction of *pure* cellulose and not with that of lignified and corky cell-walls, where in the first place higher fungi are at work, as is shown by the researches of R. HARTIG⁴⁾.

1. *The decomposition of cellulose by denitrifying bacteria.*

MEUSEL⁵⁾ states in 1871 that in the presence of cellulose bacteria

1) Bijdrage tot de kennis der cellulosegisting. Dissertation, Leonards, at Leiden, 1890, (this contains a very complete literary review).

2) Ueber die Gährung der Cellulose mit Bildung von Methan u. Kohlensäure, Zeitschr. f. Phys. Ch. Bd. 10, 1886, S. 401.

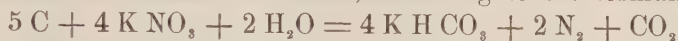
3) Sur la fermentation de la cellulose, C. R. t. 121, 1895, p. 653. — Sur un ferment de la cellulose, C. R. t. 125, 1897, p. 970. — Sur la fermentation cellulosique, C. R. t. 125, 1897, p. 1131. — Ueber die Gährung der Cellulose, Centrbl. f. Bakt. Abt. II, Bd. 8, 1902, S. 193.

4) Die Zersetzungserscheinungen des Holzes, Berlin 1878.

5) De la putréfaction produite par les bactéries en présence des nitrates alcalins C. R. t. 81, 1876, p. 533. Nitritbildung durch Bakterien, Ber. d. d. ch. G. Bd. 8, 1875, S. 1214.

reduce nitrates to nitrites; he has, therefore, proved denitrification, in the largest sense of the word, as being possible with cellulose, but from his short notes we do not understand his *modus operandi* or the nature of the cellulose used in the experiments. DEMÉRAIN¹⁾ positively states in 1897 that he has not been able to observe denitrification with flax fibres and the attention of OMELIANSKI (l.c.) has also not been attracted to this process when engaged in the study of the fermentations of cellulose. This investigator induces the methane or hydrogen fermentation by means of a nitrogenous food composed of ammonium sulphate or phosphate and sometimes he also adds asparagine, peptone, extract of meat or of manure. Strange to say, he has not worked with nitrates; had he done so, he would have noticed that the nature of the process is completely modified, for instead of the methane or hydrogen fermentation denitrification sets in which is characterised by the production of free nitrogen and carbon dioxide.

In a previous research²⁾ on accumulation experiments with denitrifying bacteria, I have shown that these aërobic organisms can oxidise many different organic substances out of contact with air with the aid of nitrates or nitrites, according to the formulae:



Denitrification was noticed with lactates, tartrates, citrates, malates, acetates, glucose, starch, asparagine, gelatin, broth, methyl and ethyl alcohol and it was, therefore, thought worth while to try whether cellulose might also be used as a source of carbon supply in the denitrification process, which indeed proved to be the case.

Before describing my experiments in detail, I will first make some remarks as to the nature of the cellulose employed. As a rule Swedish filterpaper was taken. Although this paper gives a faint blue colour with a dilute solution of iodine it was found to be very difficult to remove the impurity with boiling water; the so-called starch-free paper from SCHLEICHER and SCHÜLL, which has been purified with hydrofluoric acid, showed the same reaction. Sometimes linen tissues and cottonwool were used, from which the first also gives a blue coloration with dilute solutions of iodine, whilst the latter does not show this reaction. The little impurities, present in the cellulose employed, were however, of no moment in my experiments, as the effect on the cell walls was judged by the changes observed by a microscopical investigation.

¹⁾ Recherches sur la réduction des nitrates, Ann. agron. t. 23, 1897.

²⁾ VAN ITERSOM, Accumulation experiments with denitrifying bacteria. Proc. Acad. of Science, Amsterdam July 1902.

I obtained the best results with a paper pulp prepared by triturating Swedish filterpaper in water, care being taken that this pulp contained 2% of cellulose.

In order to obtain a thorough denitrification with cellulose, a bottle holding about 200 cc. is filled with the following mixture:

Tapwater ¹⁾ 100, paper 2, KNO_3 0,25, K_2HPO_4 0,05,

and the mixture is then inoculated with a few cc. of mud (from a ditch).

The bottle is then quite filled up in the manner described in my former communication (l.c.), to prevent access of air, and the cultivation takes place at 35°.

After the lapse of about 8 days the action is perceptible, but only after 12 days a brisk fermentation sets in. The cellulose is carried to the top by the generated gasbubbles and a quantity of liquid is forced out of the bottle by the slimy froth, while the paper-pulp is kept back by the stopper. In the beginning of the process a strong formation of nitrite may be observed, but the nitrates and nitrites soon decrease and after the lapse of about 15 days, these compounds have disappeared. The liquid is now carefully decanted from the pulp, which may be done without appreciable loss of paper fibres, as these readily agglomerate. The bottle is then refilled with the following liquid:

Tapwater 100, KNO_3 0,25, K_2HPO_4 0,05.

The process now starts much quicker than in the first cultivation, the nitrate disappears in 4 or 5 days and by repeating the operation a few times more, cultures may be obtained of an increasingly active denitrifying power, with which it is possible to completely reduce in one or two days 0.5 gram of KNO_3 dissolved in 200 cc. of water. This method of working is preferable to adding a fresh quantity of KNO_3 to the original culture, as it is then not possible to reduce on the whole more than about $\frac{1}{2}$ % of KNO_3 (calculated in regard to the quantity of the liquid used, or 25 % in regard to the cellulose) because the process then comes to a standstill by the alkaline potassium carbonate formed from the nitrate.

If now a sterilised liquid is inoculated with the strongly denitrifying rough culture and the cultivation allowed to take place under the same circumstances as described above, the action commences much more rapidly than in the first preliminary experiment, whilst the same phenomena occur. Even after repeating the inoculation ten times, no change in the intensity of the process could be observed.

Not only paper, but raw flax fibres, cottonwool and linen appeared

¹⁾ From the Downs at Loosduinen.

capable of inducing denitrification, the cottonwool, however, being attacked with great difficulty. No denitrification could be observed with sawdust or turf, whilst VAN SENU (l. c. pg. 104) has also been unable to observe decomposition of wood-cellulose by real anaerobic bacteria. This extraordinary difficult decomposition of wood-cellulose out of contact with the air, is, according to this investigator, perhaps the key to the explanation of the formation of humine substances, peat, browncoal and coal.

The distribution of the microbes, engaged in the denitrification of cellulose, in the mud from canals, seems to be a very general one, as each sample employed contained these germs. Although they are also very generally distributed in the earth, their number per cc. appears therein to be less, for, on using earth as infecting material, the action was delayed. Even in sea water, taken from the port of den Helder, were always microbes found, which in the presence of cellulose could induce denitrification; in how far these forms are similar to the terrestrial ones has not yet been ascertained, but I wish to call particular attention to the fact, that, at least near the shore, cellulose may disappear by denitrification.

The changes, which cellulose undergoes during this process, are visible to some extent with the naked eye: the white fibres soon turn orange and the pulp acquires a viscous consistency. Microscopically, it appears, that already very soon after inoculation some of the fibres are inclosed in a bacterial mucus and after a prolonged culture this is the case with nearly all the fibres. At first, the whole of the fibre is still very plainly visible within this mucus, but gradually, on account of the decomposition, it completely disintegrates into loose fibrillae and at last we only find a few particles of cellulose left, or the fibre disappears altogether (fig. 1). This destruction of the cellulose becomes very pronounced, when instead of paper-pulp strips of filterpaper are used. By repeatedly adding fresh nitrate we then finally obtain bacteria-membranes, which still have the exact shape of the strips of paper but in which we only meet isolated fibres disintegrated into fibrillae or even still more decomposed. As is already stated, the woody substance is not attacked by denitrifying bacteria, the few annulated, spiral and pitted vessels, which are contained as impurities in the filterpaper, are found unaltered in this mucus. Fig. 2 shows the form of two very strongly dissolved paperfibres (α) and some non-attacked woody elements (β , γ and δ), which are still found in such preparations.

The gases, liberated during the denitrification of cellulose and of

which some litres were collected, consist exclusively of free nitrogen and carbon dioxide; no trace of hydrogen, methane or nitrous oxide (N_2O) was found.

As regards the micro-organisms which take part in this process, a microscopical examination of the said bacterial mucus, which consists of a finely granulated substance, shows the presence of very small rod-like bacteria (fig. 1) and further there are found in the cultures infusoria, amœbae, monads, spirillae, other small bacteria and vibrionae; larger rod-bacteria or spore-forming organisms were not detected. That the bacteria, involved in the process, are no spore forming organisms, was also shown by the fact, that no pasteurised material of whatever origin (mud from a ditch or from the soil) can cause denitrification in the presence of cellulose.

Many experiments have been made with the object of isolating the bacteria taking part in the denitrification, but always with a negative result. By inoculation on meat-gelatin and cultivating at 24° , I several times obtained pure cultures of *Bacillus stutzeri* NEUM. and LEHM., which bacterium was also found in large numbers in those cases where other denitrifying bacteria were present, so that denitrification with cellulose is a new accumulation experiment for this important species, which, however, does not attack the cellulose itself.

On using meat-agar or one of the following culture liquids:

Tapwater 100, agar 2, sodium lactate 2, KNO_3 0,05, K_2HPO_4 0,05,
Tapwater 100, agar 2, glucose 2, KNO_3 0,05, K_2HPO_4 0,05,

and cultivating at 35° , other bacteria besides *B. stutzeri* were found and these were nearly always denitrifying ones. Very often a mucous colony of a motionless, non-spore forming denitrifying bacterium became conspicuous, while in other cases a small, slightly denitrifying spirillum may be isolated. No permanent denitrification with paper could, however, be obtained with any of these forms or with any combination thereof, even the crude mixture as it is formed on the plates was not capable to do this. The fact, that these bacteria may cause a temporary faint evolution of gas (which, at first, made me suspect, that the destruction of cellulose could be accomplished by ordinary denitrifying bacteria) must be attributed to the presence of small quantities of impurities in the cellulose. Still, I think we may take it for granted, that we are dealing here not with an anaërobic but with an aërobic bacterium, first of all, because all known denitrifying bacteria are aërobic and only behave anaërobically in the presence of saltpetre, secondly because methylene-blue is not reduced, when added to a medium in which cellulose is denitrifying, whilst in

cultures of the known anaërobic bacteria this compound is always decolorised. We therefore come to the conclusion, that the bacterium, which causes the denitrification of cellulose, does not grow on the used nutrient media, or else, growing there, loses immediately its denitrifying properties.

If now we compare the hydrogen and methane fermentations with the denitrifying process we find the following points of difference.

1st. In the hydrogen or methane fermentation the liberated gaseous products are carbon dioxide and hydrogen, or carbon dioxide and methane.

2nd. To those fermentations chalk must be added to neutralise the formed butyric and acetic acids, whilst in our case the saltpetre yields potassium carbonate and no volatile acids can be detected.

3rd. Those processes take place in a medium wherein sulphates can be reduced to H_2S and therefore methylene-blue is decolorised. In my experiments such a reduction of sulphates is quite out of the question as long as traces of nitrates and nitrites are still present.

4th. The methane and hydrogen fermentation are caused by comparatively large, well characterised spore forming organisms, our denitrification by very small bacteria, forming no spores.

The velocity with which cellulose disappears during the denitrification is about the same as in the methane or hydrogen fermentation of this substance. In a volume of 500 c.c., I succeeded in completely dissolving 8 grams of cellulose all but a few fibres, by means of 36 grams of KNO_3 , in a month's time. The quantity of KNO_3 theoretically required amounts to only 24 grams, but in my experiments a portion of the nitrate was lost in the expelled liquid and, therefore, more nitrate was required. By means of the hydrogen fermentation, OMELANSKI succeeded in dissolving 41.6 grams of cellulose contained in a volume of 3 litres in $3\frac{1}{2}$ months, and about 12 grams in a volume of 1 litre in 5 months, which velocities agree with the values found by me for the denitrification.

Notwithstanding the possibility of denitrification of saltpetre under the influence of cellulose, in the presence of this substance nitrification of ammonium salts and nitrites can proceed without interruption. This has already been shown by OMELANSKI¹⁾, who cultivated the nitrite ferment on paper. We also observed nitrification of ammonium salts and nitrites, when a very small quantity of cellulose (about

¹⁾ Kleinere Mitteilungen über Nitrifikationsmikroben I, Centrbl. f. Bakt. Abt. II, Bd. 8, 1902, S. 785.

0,05 %) was introduced into a thin layer of one of the following culture liquids, which were inoculated with earth:

	Tapwater	100,	NH_4Cl	0,05,	K_2HPO_4	0,05,
or	"	"	KNO_2	0,05,	"	0,05,

In my previous communication I have already pointed out, that nitrification and denitrification may take place together in garden soil and that the aëration decides, which of these processes will be the predominant one; the same conclusion may, therefore, now be drawn for cellulose as a nutrient material. A closer examination however shows, that the two processes cannot occur simultaneously in the same particle, but that a localisation must take place, in this way, that strong aëration is necessary in the particles where nitrification sets in, whilst the exclusion of air is necessary for the denitrification process.

As has already been previously observed formation of nitrite takes place in the first stage of the denitrification process in the presence of cellulose and as this substance by no means prevents the oxidation of the nitrite to nitrate, these two processes, occurring simultaneously, may cause the steady disappearance of cellulose.

We therefore see, that these same processes may cause the disappearance of cellulose in soil and in waters, which plainly shows their great importance in the "self-purification", as also in the biological purification of sewage.

2. *The aerobic decomposition of cellulose by bacteria.*

In order to demonstrate denitrification in the presence of cellulose in the manner described above, a very small quantity of this substance (about 0,05%) only must be present, for on using more say, 2% the nature of the process is completely changed. This must be attributed to a strong decomposition of the cellulose by aërobic bacteria, which then takes place and which produces a large quantity of soluble organic matter, rendering the nitrification impossible. This last phenomenon may be best observed when use is made of the following culture medium:

Tapwater 100, paper 2, NH_4Cl 0,1, K_2HPO_4 0,05, chalk 2.

Instead of NH_4Cl we may also add KNO_2 (0,1), KNO_3 (0,1), peptone (0,1) or an unlimited quantity of MgNH_4PO_4 . The cultivation takes place at 28–35° in ERLÉNMEYER flasks in a layer from 0,5—1 cm. in thickness, thus, under very aërobic conditions, so that on using KNO_2 or KNO_3 , no denitrification can be expected, at least not at the commencement.

If mud from a ditch is used as infecting material a decided growth is already noticed after 5 or 6 days, the cellulose turns to an orange colour and may even disintegrate to a thin paste after 3 or 4 weeks. Microscopically, we see, that we obtain besides the cellulose-dissolving bacteria a very rich accumulation of spirillae, which however do not themselves attack cellulose. I have often repeated these experiments and always with the same result: the cultures become extremely rich in spirillae and these consist of many varieties. As a rule different species were found in a same culture, large spirillae with several windings in company with small, very mobile ones, but sometimes it also happened, that it looked under the microscope, as if we were dealing with pure cultures of special spirillae. These different results being no doubt connected with the nature of the germs in the infecting materials employed. Often however, we meet besides the spirillae, infusoria, monads, amoebae and small forms of bacteria, sometimes also rod bacteria and spore forming organisms, but the spirillae are always in the majority.

If such cultures are transported into the same sterile medium, the chief character remains the same, but the growth takes place more rapidly and as a rule the number of species of spirillae is much reduced, so that frequently but a single one remains. Here it is perhaps the proper place to state, that an accumulation of spirillae may also be obtained in using a nutrient liquid composed as follows:

Tapwater 100, calcium lactate 2, peptone 0.05, K_2HPO_4 0.05,

which is infected with a small quantity of ditch-mud.

At temperatures from 28 -37° exceedingly rich spirillae cultures are formed in this liquid. It would, however, be too rash thence to conclude, that lactate is formed as a transient decomposition product of the cellulose.

The destruction of the cellulose is not only apparent from the strong growth of microbes, but also from a microscopical examination of the fibres. As in the case of the denitrification process, these are here also found to be enveloped with a bacterial mucus in which is always found a very small rod-bacterium, and occasionally a large micrococcus, which itself does not attack cellulose, but much accelerates its dissolution by the small bacterium. The destruction is no doubt caused by the latter, for sometimes, we have obtained cultures, which exclusively contained this species only.

That the decomposition is here an aërobic one, is shown by the fact, that it commences at the surface of the culture and also takes place equally well when we cultivate in a very thin layer.

Owing to the dissolution of the cellulose the absorption of oxygen in the cultures may become so strong, particularly when working with thick layers of cellulose paste, that anaërobic processes become possible. If, now, nitrates or nitrites are still present in the culture denitrification will set in, but if these compounds are already decomposed, or if originally another source of nitrogen had been added, methane or hydrogen fermentation becomes possible. In the last case we microscopically observe the very characteristic rods with spores, accumulating on the fibres. In this anaërobic stadium the spirillae are for the greater part expelled but the destruction is now much more intense than when it took place exclusively under aërobic conditions so that in a short time the paper pulp gets for the greater part dissolved and leaves behind a bacterial mucus.

When using as infecting material soil, instead of mud from a ditch, we observe on the whole the same phenomena, only we do not find then that variety in species of spirillae noticed with ditch-water. As a rule a short, thick, granulated spirillum with one half winding is then conspicuous and I have succeeded in preparing pure cultures of this species, already observed previously ¹⁾.

An experiment with sea water showed, that this also causes the aerobic decomposition of cellulose and an accumulation of different species of spirillae was obtained at the same time. In this case the decomposition in the anaërobic stadium may also be caused by an anaërobic spore forming organism, which much resembles the bacteria of the methane and hydrogen fermentations but still presents a different shape.

I have tried to isolate the bacteria connected with the aërobic destruction but was not more successful than in the denitrification experiment. On sowing on broth-gelatin or broth-agar a number of bacteria species were found: *fluorescents*, *B. coli commune*, *B. subtilis*, *B. mesentericus* and several others unknown to me, but none of these species or none combination thereof was capable of attacking cellulose.

Our result that cellulose may be attacked by aërobic bacteria widely occurring in nature, is confirmed in a particularly convincing manner by the following experiment:

In a glass box are placed two discs of Swedish filterpaper between which has been sprinkled a little quantity of powdered $MgNH_4PO_4$; the paper is imbibed with a solution of 0.05 gram of K_2HPO_4 in 100 cc. of tapwater. If now we introduce upon the plate thus prepared a little

¹⁾ BEIJERINCK. Ueber oligonitrophile Microben. Centrbl. f. Bakt. Abt. II, 1901 Bd. 7, S. 574.

quantity of water containing in suspension humus, garden soil or, still better, ditch-mud, and if we cultivate at $24-28^{\circ}$, the paper gets covered after 4 or 5 days with yellowish-brown spots which, microscopically, are found to consist of bacteria. These spots spread with great rapidity, and it is highly interesting to observe how in a short time the white filterpaper is covered with the rusty culture. This is accompanied by a decided decomposition of the paper fibre, which is shown in the first place by the fact that the paper becomes quite soft and pulpy just on the spots exposed to the action of the brown bacterium, losing there all coherence and sinking down along the edges of the phosphate. The phenomenon becomes still more pronounced, when instead of filterpaper, linen or cotton is used; after about 10 days, the affected spots of the originally strong material have lost all power of resistance and after 15 days large holes will be formed when carefully pouring water on them.

Microscopically, it appears that a powerful destruction of the fibre is taking place (fig. 3) due to the action of a brown, very mobile, little rod bacterium (*Bacillus ferrugineus* fig. 4). The fibre is again enveloped by a mucus in which is found, in many cases, the same micrococcus as mentioned above (fig. 5 and 6). Owing to the combined action of these two bacteria the fibre may disappear completely and leave behind a mucus containing only micrococci; we then obtain an image as shown in fig. 7. In addition to amoebae and monads other small bacteria are found, but there is no question of the presence of anaërobics, which occur in the hydrogen or methane fermentations, the action being a purely aërobic one and taking place very well in filterpaper both sides of which are exposed to the air.

On transferring the brown spots to previously sterilised paper discs, between which MgNH_4PO_4 has been sprinkled and which have been saturated with a sterile 0,05% solution of K_2HPO_4 , the phenomenon remains constant. On inoculating them into the above described cellulose pulp a culture is obtained resembling that which arises by the direct action of ditch-mud or earth, but no spirallae are found this time, for these being microaerophilous cannot grow in the aërobic culture on the paper discs. On the other hand the cultures from paper pulp were occasionally capable of producing brown spots on paper discs, showing that in both cases the destruction of the cellulose may be caused by the same microbe. I also noticed a few times that the discs were covered with colorless spots caused by a larger mucus-secreting rod, and as moreover the paper pulp cultures often are only little colored, it must be assumed, that the aërobic

decomposition of cellulose may be caused by two microbes at least, but among these the brown pigment bacterium is the most conspicuous.

On using sea water as infecting material, similar brown spots were observed. When these were transferred to paper without addition of 3% NaCl they caused no destruction, which shows that we are dealing here with a specific sea bacterium.

I have made several experiments with various culture materials in order to isolate this very interesting cellulose-destroying brown pigment bacterium, which I was particularly anxious to accomplish after having observed, that the crude bacteria-mixture as grown on different culture media often again produces spots when spread over paper, which shows that on these media the said bacterium had kept alive. But I was again unsuccessful in isolating a species which either alone or in combination with other bacteria was capable of causing the brown spots on paper. Though I succeeded in isolating from these spots a brown and a yellow bacterium, which as a rule, were present in large numbers, yet, as in the case of the denitrification process, no destruction of cellulose could be induced by their pure cultures. The explanation of this circumstance has not yet been found.

The aërobic destruction of pure cellulose and also the more difficult destruction of the lignified cell walls,¹⁾ on which we cannot enter in this investigation, must, like the denitrification (which is only possible with non lignified cellulose and takes place out of contact with air) play an important part in the disappearance of vegetable substances in nature. The well known fact that wooden piles, when partly immersed in water are attacked exactly at the place of contact between the water and the air, the breaking of ropes, when suspended in water, exactly at its surface and also the aërobic decay of wood must be attributed mainly to the action of aërobic destroyers. VAN SENUS (l. c. 103) who was acquainted with these facts, did not deny the possibility of a decomposition by aërobic bacteria but thought it very unlikely "as no phenomenon ever pointed to such a fact."

That the above-described yellowish-brown pigment bacterium plays indeed an important part in the disappearance of the cellulose, is shown by the following experiment.

On October 14, 1902 were buried in the garden of the bacteriological laboratory at about 15 c. m. below the surface a linen cloth with a red colored border, and in two other places four sheets of filterpaper, all in a horizontal position. Left in the soil untouched during the recent winter and on exhuming them March 22, 1903

¹⁾ The great stability of wood-cellulose towards microbial life is directly opposed to the ready decomposition of wood paper under chemical influences.

not a trace could be found of the filterpaper, whilst the linen cloth had become soft and pulpy, had lost all coherence and could only be removed from the soil in pieces; the red border, however, had retained its original structure. The originally white tissue had assumed the same yellowish-brown colour so familiar to me from the cultures on the paper discs, while on microscopical investigation the fibres appeared to be much decomposed and disintegrated into fibrillae and besides moulds and amoebae only small bacteria were observed. On putting some of the well-cleaned fibres on the paper discs prepared as described above, I obtained after three days the rapidly spreading, yellowish-brown spots of the destructive, small, rod-shaped pigment bacterium. A cellulose-destroying mould, *Mycogone puccinioides*, also could be isolated from the linen, but the fact that the yellowish-brown pigment bacterium was here predominant, could not be doubted.

3. The decomposition of cellulose by moulds.

The fact that cellulose may be attacked by certain fungi has been first stated by DE BARY ¹⁾ for *Peziza sclerotium*, and the same was found by KISSLING ²⁾ and by MARSHALL WARD ³⁾ for a kind of *Botrytis*, by BEHRENS ⁴⁾ for *Pseudodematophora*, *Botrytis vulgaris*, *Cladosporium herbarum* and *Aspergillus glaucus*. This last investigator did not notice any decomposition by *Mucor stolonifer*, *Penicillium glaucum* and *Penicillium luteum*. KOHNSTAMM ⁵⁾ prepared a cellulose-destroying enzyme from *Merulius lacrymans* the common wood fungus. WENT ⁶⁾ has shown, that *Monilia sitophila*, the "ontjom" mould from Java, is capable of digesting cellulose and KONING ⁷⁾ has found that one of the

¹⁾ Ueber einige Sklerotien u. Sklerotienkrankheiten, Bot. Zeit. 1886, S. 377.

²⁾ Zur Biologie der *Botrytis cinerea*, Diss. Dresden, 1889.

³⁾ A lily disease, Annals of Botany, Vol. II, 1888/89, p. 346.

⁴⁾ Trockene u. nasse Fäule des Tabaks. Der „Dachbrand“, Zeitschr. f. Pflanzenkr. Bd. III, 1893, p. 84. — Untersuch. über den Wurzelschimmel der Reben, Centrbl. f. Bakt., Abt. II, Bd. 3, 1897, S. 584. — Beiträge zur Kenntniss der Obstfäulnis, Centrbl. f. Bakt. Abt. II, Bd. 4, 1898, S. 514. — Unters. über die Gewinn. der Hanffaser durch natürl. Röstmethoden, Centrbl. f. Bakt. Abt. II, Bd. 8, 1902, S. 114.

⁵⁾ Amylolytische, glucosidsplattende, proteolytische u. cellulose lösende Fermente in holzbewohnenden Pilzen. Beihefte z. Bot. Centrbl. Bd. 10, Heft 2, 1901., S. 90.

⁶⁾ The influence of feeding on the secretion of enzymae by *Monilia sitophila*. Proc. Jan. 1901. — Ueber den Einfluss der Nahrung auf die Enzyymbildung durch *Monilia sitophila* (MONT) SACC. Jahrb. f. wiss. Bot. Bd. 36, Heft 4, S. 643.

⁷⁾ Genootschap 1er Bev. v. Natuur- en Heckkunde Amsterdam, 2 series, dl. IV, Afd. 5, Zitting 7 Dec. 1901.

most common humus-inhabitants from the forest of Spanderswoude, *Trichoderma koningii*, possesses the same property.

We have succeeded in finding an experiment by means of which the cellulose-destroying moulds may be isolated from nature in a direct and certain manner. Two sterile discs of Swedish filterpaper are placed in a glass box and moistened with the following liquid:

Tapwater 100, NH_4NO_3 0,05, KH_2PO_4 0,05.

As infecting material earth or humus may be used, but the best results are obtained by simply exposing the opened box for about 12 hours to the open air. If then we cultivate at 24° and take care to keep the paper moist, colonies of moulds already become visible after 5 or 6 days, but it is only after 14 days or three weeks, that we notice the enormous richness of these cultures, and then we are surprised at the great number of mould species, which make their appearance. Many kinds which we seldom or never notice on malt-gelatin are found in large numbers on these paper discs. These species certainly are also capable of growing on malt-gelatin, but their germs, as they occur in nature, apparently find thereon an unfavorable soil. Another advantage of the cultivation on paper is that it is particularly favorable to the formation of perithecia and pycnidia, which do not readily develop on rich soils ¹⁾.

From these culture experiments it appears that a continuous rain of spores from cellulose-destroying moulds falls in the garden as well as in the rooms of the bacteriological laboratory. For instance on March 11, when the weather was dry whilst the earth was moist, 152 cellulose-destroying moulds were collected on a plate of 275 c.m. square, after this had been exposed for 12 hours to the open air, and among these moulds about 35 species were recognised. As these germs must continually drop on the soil, it might be expected that the latter would be remarkably rich in living moulds and it appeared from experiments, that this is really the case at the surface of the garden soil, but in a much less degree than might have been expected, while lower down in the soil the number of moulds seems to be still less. From this it follows that most of the spores, which fall on the earth rapidly die off.

In order to prepare a pure culture of the fungi isolated by the "paper-experiment" some material from the raw cultures was transferred to malt-gelatin, where it appeared that the moulds were generally much contaminated with bacteria, from which however,

¹⁾ Compare MOLLARD, Rôle des bactéries dans la production des périthèces des *Ascomolus*, C. R. t. 136, 1903, p. 899.

they could be freed by another inoculation. These bacteria are saprophytes which do not attack cellulose but grow at the expense of the products generated by the action of the moulds on cellulose. This result was not unexpected for, as stated in the preceding paragraph, the cellulose-destroying bacteria live in a faintly alkaline medium, whilst in the case of moulds the reaction is acid, owing to the presence of KH_2PO_4 . In order to be perfectly certain of the pureness of the moulds, cultures from the spores were finally made on malt-gelatin.

The following species, which were detected in these cultures, have been submitted to a closer examination:

1. *Sordaria humicola* OUD.
2. *Pyronema confluens* TUL.
3. *Chaetomium kunzeanum* ZOPF.
4. *Pyrenochaeta humicola* OUD.
5. *Chaetomella horrida* OUD.
6. *Trichocladium asperum* HARZ.
7. *Stachybotrys alternans* OUD.
8. *Sporotrichum bombycinum* (CORDA) RABH.
9. " *roseolum* OUD. en BELJER.
10. " *griseolum* OUD.
11. *Botrytis vulgaris* FR.
12. *Mycogone puccinioides* (PREUSS) SACC.
13. *Stemphylium macrosporoideum* (B. en BR.) SACC.
14. *Cladosporium herbarum* (PERS.) LINK.
15. *Epicoccum purpurascens*. EHRENB.

In the determination of these species, of which Nos. 9¹⁾ and 4, are new, we have been kindly assisted by Prof. Dr. C. A. J. A. OUDEMANS, to whom we have to express our thanks.

In order to form an opinion on the destruction of cellulose by the isolated species, and also to study their fructification, pure cultures were inoculated on paper discs, which after sterilisation, were drenched with the above-named solution. Instead of merely placing the spores on the paper, it was found desirable to push them in it by means of a platinum wire and then to reduce the spots there to pulp. The cultivation is made at 24°, care being taken to keep the paper moist, for which it was found advantageous not to use water only but the said liquid, as the nitrogen in particular is rapidly used up. The above-named moulds all grow over the paper discs, form their fructification-organs in a very characteristic manner and often produce intensively colored, brown, black and red pigments, which are absorbed by the paper

¹⁾ Nederl. Kruidkundig Archief, Januari, 1903.

fibre. Interesting are the cultures obtained in this way of *Chaetomium kunzeanum*, which sometimes produces a carmine-red pigment and which forms dark red peritheciae, the asci of which contain eight grey spores; those of *Chaetomella horrida*, which forms delicate black hairy pyrenidia, and particularly those of *Pyrenochaeta humicola*, which produces an intense black pigment, stable towards acids and alkalis, and which communicates a dark colour to the fibres, quite resembling the humus coloring matters. This latter species however, grew more readily on an alkaline medium, so that we preferred in this case the said drenched paper discs, between which $\text{Mg NH}_4 \text{PO}_4$ had been sprinkled. An interesting culture is also that of *Sordaria humicola*, as this ascomycete is only then capable of forming perithecia on paper discs, when these give no longer any reaction on ammonia or nitrates. Besides the above-named species, a luxurious growth was obtained of *Trichocladium asperum*, *Mycogone puccinioides* and *Stemphylium macrosporoides*, which three species exhibit great similarity both in their morphological and physiological properties. *Epicoccum purpurascens* also grew strongly on the paper and formed a purple-red pigment. This species I met several times in the air and also (in company with *Cladosporium herbarum*) on half decayed leaves of *Populus balsamifera*.

Cultures of these moulds were not only made on paper discs, but also on cellulose in ERLÉNMEYER flasks, into which was introduced a thin layer of the following culture liquid:

Tapwater 100, paper-pulp 2, $\text{NH}_4 \text{NO}_3$ 0,05, $\text{KH}_2 \text{PO}_4$ 0,05.

In this case a repeated addition of $\text{NH}_4 \text{NO}_3$ proved very advantageous. On the pulp the cellulose-destroyers grow still better than on the paper discs and in 3 or 4 days the cellulose is converted by the mycelium into a coherent mass. Afterwards, the fructification organs appear, and with *Botrytis vulgaris* even formation of sclerotia was observed.

The destruction of the cellulose may be regarded as certain when strong growth on the paper discs and on the paper pulp are being observed. The impurities contained in the paper may also cause a slight growth of moulds which do not attack cellulose, but these soon cease to develop. The decomposition may be seen very clearly by a microscopic examination of the cultures on filter-paper, when these have stood a long time. It will then strike us how a large number of fibres have suffered a process of dissolution; sometimes pores are formed perpendicularly to the direction of the fibre, sometimes the fibres have disintegrated into fibrillae. Fig. 9

of our illustration shows the image of the destruction by *Mycogone puccinioides*, in which the structure of the fibrillae and the said pores are visible.

The degree of destruction also may be ascertained by direct weighing. A culture with *Mycogone puccinioides* was made on a double disc of filterpaper, two equally heavy filters serving as control. After a culture, lasting 40 days, the discs, from which the strongly developed mycelium was not removed, weighed 1.00 gram, whilst the controlling discs weighed 1.16 gram, showing that about 14% of the cellulose had disappeared. A similar experiment with *Trichocladium asperum* gave a loss of 9%. These great losses only can be explained by the oxidation of the products derived from the cellulose under the influence of the respiration process. The oxidation of cellulose also was studied with filterpaper pulp, namely by weighing the amount of carbon dioxide, liberated during a culture of *Chaetomium kunzeanum*. In this experiment an oxidation of about 4% of the cellulose could be noticed after a 28 days culture, a quantity large enough to remove all doubt about the destruction of the cellulose.

No, growth or only a very small one, was observed when cultivating the moulds on:

Tapwater 100, agar 2, NH_4NO_3 0,05, KH_2PO_4 0,05,

but as soon as cellulose was added a strong development set in, showing in a surprising manner, that agar is a less nutrient food for these moulds than cellulose. The cellulose used in these experiments must be very finely divided and was prepared by treating cottonwool with concentrated hydrochloric acid, which causes the cotton fibres to break up into very small fragments. A preparation, which appeared to be still more suitable was prepared as follows: Paper which has been converted into soda-cellulose by the action of strong soda-lye, is readily soluble in sodium xanthogenate to a light yellow liquid: the "viscose" of CROSS and BEVAN¹⁾, which is purified by precipitation with alcohol; on adding hydrochloric acid to its aqueous solution cellulose is precipitated in a very pure condition. I have to thank Mr. DE JONGH SCHEFFER, for a specimen of this preparation, which he prepared in the chemical laboratory of the Polytechnic School at Delft.

I found that, when cultivating on this agarcellulose, the growth entirely depends on the quantity of the cellulose added: with much cellulose a strong growth was observed.

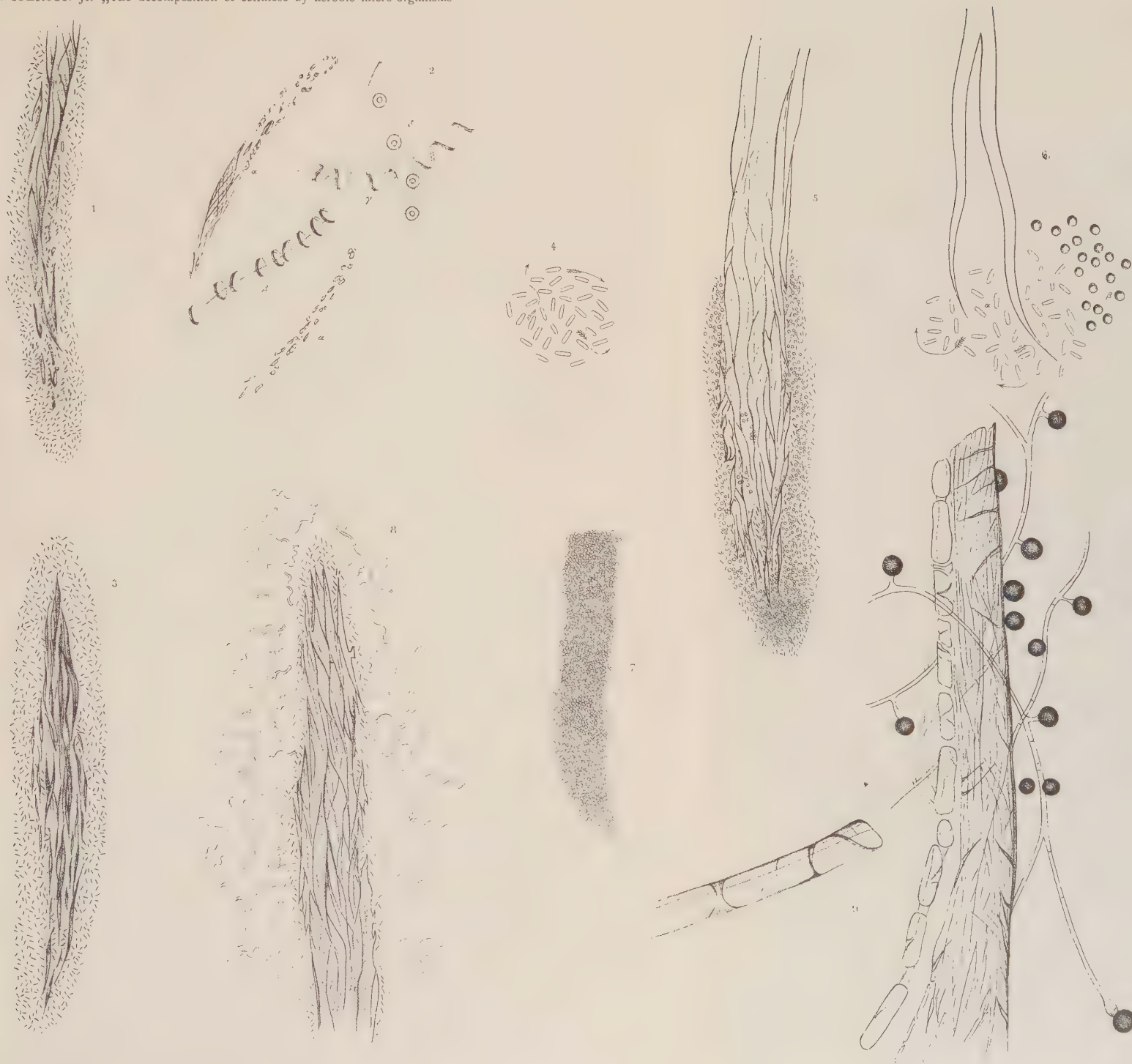
¹⁾ CROSS and BEVAN, *Cellulose*, 1895, p. 25. London, Longman Green and Co.

As in the case of the moulds investigated by the above-named observers, also the species employed by me showed the presence of an enzyme, which dissolves cellulose and to which the name of "cellulase" may be given ¹⁾. If cultures on cellulose pulp were treated with chloroform, the liquid, after being freed from chloroform by evaporation, appeared capable of reducing FEHLING's copper solution. If the culture had been boiled before being treated with chloroform, no reduction took place. From these last experiments, which were conducted similarly to those of BEHRENS (l.c.), it appears that the moulds only produce the quantity of reducing matter necessary for their growth and no more. That the quantity or the nature of the enzyme secreted by the moulds differs considerably, is shown by the great difference in destructive power, as may be readily observed from the growth on the paper discs and from the dissolution of the cellulose in the paper-pulp cultures. To the powerful destroyers belong: *Trichocladium asperum*, *Mycogone puccinioides*, *Stemphylium macrosporoïdeum*, *Chaetomella horrida*, *Botrytis vulgaris*, *Epicoccum purpurascens*. To the moderately strong ones: *Chaetomium kunzeanum*, *Stachybotrys alternans*, *Cladosporium herbarum*, *Pyrenochaeta humicola*, *Pyronema confluens*. To the weak ones: *Sordaria humicola*, *Sporotrichum bombycinum*, *Sp. roseolum*, *Sp. griseolum* and *Aspergillus niger*. No destruction was noticed with *Mucor stolonifer*, *Mucor mucedo*, *Dematium pululans* and *Rizopus oryzae*.

Summary of results.

1. Cellulose may be made to dissolve by the action of denitrifying, non-sporeforming aërobic bacteria provided there be an *limited* supply of air.
2. Although nitrification cannot take place in the presence of a somewhat large quantity of soluble organic matter, cellulose does not affect this process in case of sufficient aëration.
3. The combined action of nitrification and denitrification must play an important part in the disappearance of cellulose in nature, for instance in the self purification of waters and of the soil, as also in the biological purification of sewage.

¹⁾ This name, already used by KOHNSTAMM (l.c.) is preferable to the name *cytase* which has been used by BROWN and MORRIS (Journal of Chem. Soc. 57, 1890, p. 458) for the cellulose-dissolving enzyme in germinating seeds and should according to METSCHNIKOFF (Ann. Inst. Pasteur, 1899, t. 12, p. 737) be given to an alexin occurring in normal serum.



4. Cellulose may also be attacked, when there is a full supply of air by widely distributed, aërobic, non-sporeforming bacteria, among which a brown pigment bacterium (*B. ferrugineus*) is predominant. The destruction is particularly strong in symbiosis with a yellow micrococcus, which itself is inert.

5. Extraordinarily rich spirillae cultures are formed in nutrient liquids in which cellulose is being attacked by aërobic bacteria after infection with ditch-mud or garden soil. Probably the distribution of the spirillae in nature is mainly governed by cellulose.

6. The property of moulds to attack cellulose is a very common one. The dissolution is due to a specific enzyme to which the name of "cellulase" may be given.

7. One of the causes of the origin of humus coloring matters is the formation of pigments from cellulose by bacteria and moulds.

This investigation has been made in the bacteriological laboratory of the Polytechnic School under the guidance of Prof. BEIJERINCK.

Delft, March 1903.

EXPLANATION OF THE FIGURES.

Fig. 1. Fibre of filterpaper with denitrifying bacteria, disintegrated into fibrillae, enclosed in mucus. Enlargement 550.

Fig. 2. Debris of filterpaper at the end of the denitrification process, most of the fibres are dissolved. α the last debris of cellulose fibres, β , γ and δ nonattacked elements of "woodcellulose". Enl. 100.

Fig. 3. Fibre of filterpaper with aërobic bacteria disintegrated into fibrillae, enclosed in mucus. Enl. 550.

Fig. 4. Bacterium from the preceding figure more strongly enlarged; arrows represent motion. Enl. 1500.

Fig. 5. Fibre of filterpaper attacked by an aërobic bacterium with saprophytic micrococcus, commencing to disintegrate into fibrillae. Enl. 550.

Fig. 6. Two fibrillae of the preceding fibre more strongly enlarged, with α aërobic destructive bacteria and β saprophytic micrococcus. Enl. 1500.

Fig. 7. End of the destruction in fig. 5 the fibrillae having become invisible; micrococci only visible. Enl. 550.

Fig. 8. Fibre attacked by aërobic bacteria, disintegrating into fibrillae and enclosed in a thin mucous layer as medium for a spirillae culture in which 3 species are recognisable. Enl. 550.

Fig. 9. Destruction of a fibre of filterpaper by *Mycogone puccinioides*, besides the fibrillary structure, cross pores have been formed in the fibrillae owing to the action of the cellulase. Enl. 550.

(May 27, 1903).

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